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TRANSLITERATION

There is no ideal system of transliterating Russian; each has its advantages and disadvantages. For the translation of Geokhimiya we have chosen the system used by Chemical Abstracts, partly because of its wide acceptance by other journals and partly because of certain advantages in alphabetization of names. The principal differences between this system and others in common use are as follows:

Russian	Chem. Abs.	Others
Х	kh	h
Ц	ts	tz
Щ	shch	sch
Ю	yu	iu
Я	ya	ia

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THE SOLUBILITY OF WATER IN BASALTIC AND GRANITIC MELTS

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More than a quarter of a century ago, R. Goranson published the first quantitative data on the solubility of water in silicate melts of granitic and feldspathic composition as a function of temperature and pressure [1, 2].

The results of his investigation laid the foundation for the development of many general and specific ideas concerning the behavior of magmatic volatite constituents and of magma itself.

At present, Goranson's work is the only systematic experimental study of the solubility of water in acid and alkalic silicate melts.

There are no analogous quantitative data elucidating the relationship between water, the principal volatile constituent, and melts with the composition of basaltic magma which would permit a comparison between the solubility of water in acid and basic melts. Such experimental data are the more necessary because of the primary nature of basaltic magma. Moreover, the relations between the volatile fraction and the melt are the determining factors in the development of magmatic activity leading to the formation of rocks as well as ores.

That the experimental data needed for the solution of this problem have not been obtained until now must be ascribed to the considerable technical difficulty involved in experimentation.

The present experimental investigation was undertaken to obtain these data.*

The basis for the setup used in the first group of experiments, those described in the present paper, was the theoretical scheme worked out by B. A. Korndorf and N. I. Khitarov. In the course of assembly, some of the individual parts of the apparatus were modernized and the conditions of experimentation worked out.

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*In addition to the authors, laboratory technicians P. V. Boitsov and E. E. Filippova took part in the investigation.

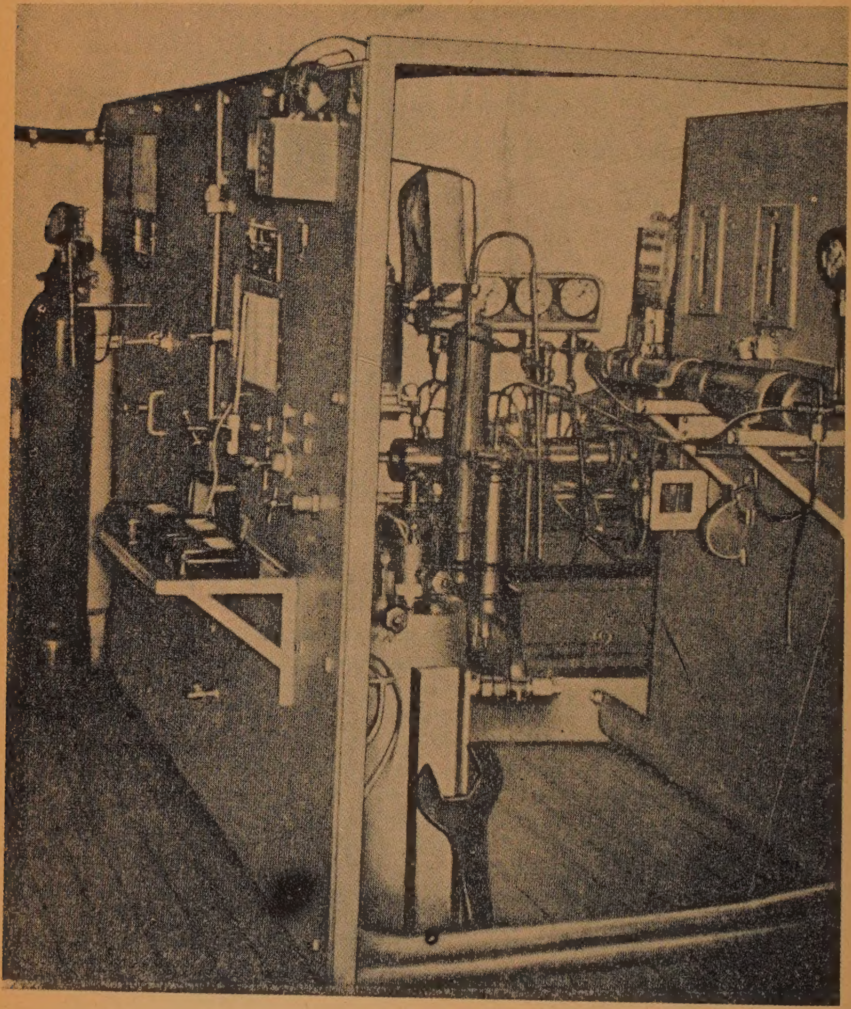

Fig. 1. General view of the apparatus

Apparatus

The apparatus used in the experimental investigation is a high pressure vessel with an internal furnace. A general view of the setup is given in Fig. 1 and a diagram of its principal part, in Fig. 2.

The process under investigation takes place in the reaction chamber, 3. It is made with thin walls and relieved of mechanical stress by the equalizer

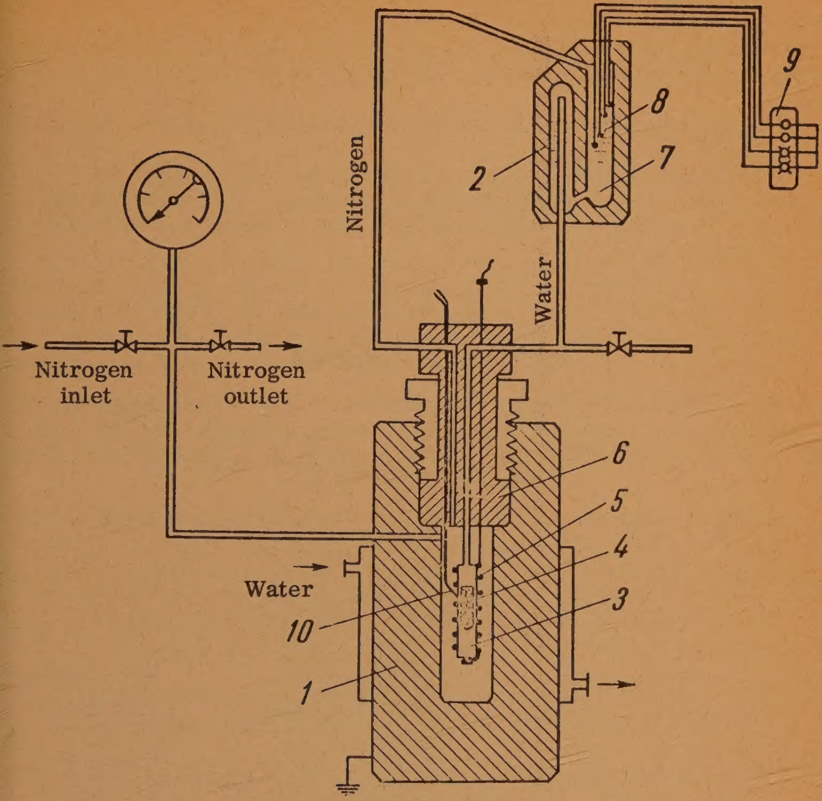

Fig. 2. Diagram of the principal parts of the apparatus

1 -- high pressure vessel, 2 -- equalizer, 3 -- reactor, 4 -- sample tube, 5 -- resistance furnace, 6 -- lid, 7 -- Wood's metal, 8 -- electric leads, 9 -- signal lamps, 10 -- thermocouple

of external and internal pressure, 2. The reaction chamber is subjected only to the effects of high temperature generated by the resistance furnace. The equalizer is a U-shaped vessel filled to a certain level with Wood's metal, which separates water from the nitrogen occupying the rest of the system. A signal arrangement indicates the level of the melt, which is kept at a definite height by the valves regulating the volume of nitrogen.

The reaction chamber is placed in a thick-walled vessel surrounded by a water jacket, 1. During the experiments this vessel remains cold.

The required water vapor pressure was produced by feeding water into he reaction chamber under pressure and heating it. The counter-pressure was maintained by nitrogen passing through a gas compressor equipped with a multiplying-piston arrangement.

The temperature was measured by a platinum-platinum-rhodium (10%

rhodium) thermocouple with its junction within the reaction chamber. The thermocouple was systematically checked.

The reaction chamber and the furnace are contained in a special small cylinder which serves as a screen, convection current damper and thermal insulator.

By special investigations conditions were found which reduce convection to a minimum.

The temperature variation along the axial zone of the sample tube was ± 15-20°C; at the point of sampling it was maintained consistently within ± 5°C. The pressures were measured by a high pressure Bourdon type gauge to within 1%.

Experimental Procedure

The powdered material under investigation (7-8 g) was loaded into special alundum tubes 9 mm in diameter and 70 mm in length (Fig. 3). The powder was moistened with distilled water, strongly compacted and placed

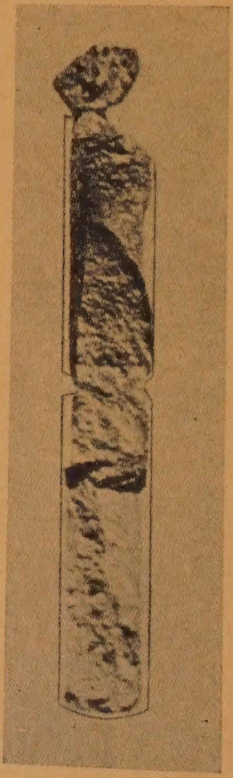

Fig. 3. Alundum tube with quenched melt

in the reaction chamber. The position of the tube was half way up the reaction chamber. The top of the tube was covered with a cylindrical lid occupying the entire upper part of the reaction chamber to the capillary. The end of the thermocouple was located in the body of the reaction chamber near the middle of the tube.

The samples were held at the preset temperature and pressure for 2-1/2 and 5 hours. Inasmuch as experience showed that the difference in time had practically no effect on the results, in later experiments the temperature and pressure were maintained for the preset values for 2-1/2 hours.

Under constant pressure, the sample usually cooled to 700°C in 2-2-1/2 minutes and to 600°C in 3-3-1/2 minutes from the time the furnace was switched off. When the temperature reached 500°C the pressure was gradually reduced as the sample cooled to 150-200°C. This procedure gave the best retention of water in the melt.

Water Determination

Water was determined in crushed material. Fractions 0.25 to 0.5 - 0.7 mm in size were selected. Samples weighing 200 to 370 g were placed in a platinum boat and hygroscopic water was determined by holding them at 105°C for 15 minutes. The time of heating was limited because additional observations showed that occasionally water diffused noticeably even at 105°C. This was noted by Goranson for glasses synthesized at high pressure.

After moisture determination, the combined water in the sample was determined by absorption in anhydrone in Pregl tubes in the apparatus shown in Fig. 4.

The samples and the Pregl tubes were weighed on a semimicrobalance

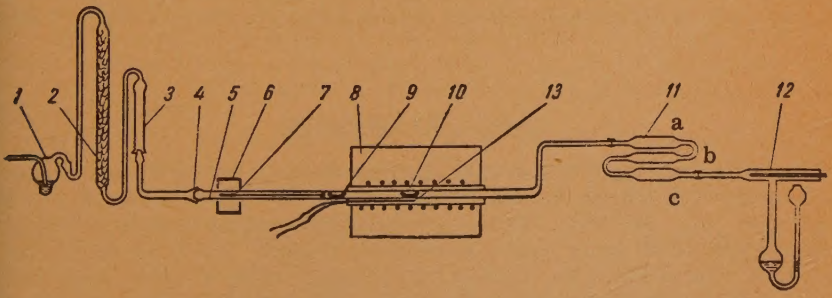

Fig. 4. Apparatus for determination of water

1 -- bubble counter, 2 -- tube with $CaCl_2$, 3 -- tube with anhydron, 4 -- ground joint, 5 -- silica tube, 6 and 7 -- electromagnet with a plunger, 8 -- furnace, 9 and 10 -- platinum boat in two positions, 11 -- Pregls tube with anhydrone (a, b, c), 12 -- rheometer, 13 -- thermocouple

of the ADV-200 type to the nearest 0. 05 mg. The 200-370 g samples were weighed to within 0. 1 mg, so that the error of determination was from 0. 05 to 0. 03 mg.

The platinum boat with the sample was placed in the cold end of the quartz tube (position 9). A Pregl tube (c) with a rheometer attached to it was joined to the other end of the quartz tube. The furnace was turned on, and when temperature reached 200°C a stream of air was passed through the apparatus at a definite rate by means of an aspirator. After the apparatus had dried for two hours, the temperature in the furnance was allowed to drop to 105°C and the boat was moved by means of a magnet into the middle part of the quartz tube lying in the furnace (position 10). With the air stream flowing at a uniform rate, the weighed Pregl tubes a and b were joined to tube c. The temperature of the furnace was slowly raised to 1200°C and held there for 30 minutes. After this the furnace was turned off and the tubes, a and b, were disconnected and weighed.

Material for the Experiments

In the experiments we used a standard sample of basalt from the Laboratory of Volcanology kindly provided by V. I. Vlodavets and described by him as the most basic type of lava extruded in the region of Klyuchevskii volcano up to 1932 [3]. This basalt was taken from the lava flow of the parasitic cone of the Klyuchevskii volcano called the Kirgurich (1932).

Both macroscopically and microscopically the rock is fresh and contains no secondary minerals. The phenocrysts, olivine (2V = +89°) and pyroxene (2V = +58°; c: Z = 38°) (diopside) are set in a microgranular groundmass with glass.

The groundmass is composed of small grains of clinopyroxene, minute grains of ore minerals, thin microlites of calcic plagioclase and brown semitransparent glass with N = 1,507--1.510 ± 0.002.

For the experiments with granitic melt we used the El'dzhurtinskii porphyritic biotite granite (Northern Caucasus) with large phenocrysts of plagioclase (oligoclase and albite-oligoclase), potash feldspar, quartz and biotite. The chemical composition of basalt and granite is given in Table 1

Results and Discussion

The tubes remained intact after the experiment. Along the walls the microscope sometimes showed a fused film hundredths of a millimeter in thickness (Fig. 3). When the tubes were split open the samples of quenche melts appeared as glass rods with vitreous luster. The material for the determination of the water content was selected under a binocular microscope from the central parts of the rods. The rest of the sample, together with the fragments from the central area, was made into thin sections.

The solubility of water in basaltic and silicate melts was determined at temperatures up to 1000°C and pressures up to 3000 kg/cm².

Two series of experiments were made with the basalt in order to determine the solubility of water in it at T = 900°C and P = 3000 kg/cm². In one series, the sample was heated at 1000° for one hour, cooled to 900°C and held at this temperature for 2-1/2 hours. In the other, the sample was

Table 1

Chemical Composition (%) of the Kirgurich Basalt and El'dzurtinskii Granite

Composition	Basalt	Granite	Composition	Basalt	Granite
SiO_2	52,05	72,58	Na_2O	2,46	3,17
TiO_2	0,82	0,35	K_2O	0,89	4,37
Al_2O_3	15,16	14,11	P_2O_5	0,13	0,11
Fe_2O_3	4,48	0,57	S	—	0,03
FeO	5,16	1,53	F	—	0,06
MnO	0,10	0,04	H_2O^-	0,03	0,08
MgO	9,49	0,65	H_2O^+	0,06	0,49
CaO	9,29	1,72	CO_2	—	0,02
				100,12	99,88

Note: Comma represents decimal point.

heated to 900°C and held at that temperature for 2-1/2 hours.

This gave the most reliable range of water content in the melt corresponding to the preset temperature and pressure. As has already been stated, the experiments were made not on basaltic glass but on the powdered natural basalt in order to avoid changing the original composition by preliminary melting. Moreover, this method made it possible to obtain data on the stability of individual minerals.

The work wigh granite was also done on the powdered natural rock.

The results of the experiments with granite and basalt for different temperatures and pressures are presented in Tables 2 and 3.

Goranson's data on the solubility of water in granitic melt under similar T and P obtained in experiments with granitic glass differ from the data given above. There are two main reasons why it would be incorrect and undesirable to compare the two sets of data: first, the granites used in the two experiments were different and so was the preparation of samples; and, second, the experimental approach was quite different, beginning with the weight of the samples, which was only from 50 to 150 mg in Goranson's experiments, or less than one hundredth of the weight of samples used in the present research.

Judging by the figures for the 900°C isotherm, the solubility of water in the glass prepared from the granite of Stone Mountain, as determined by Goranson, is one and a half times greater than the solubility of water under analogous conditions in the molten El'dzhurtinskii granite.

The data for the El'dzhurtinskii granite appear to be nearer the actual solubility of water in granitic melts in general if the recent results of Jahns and Burham are considered [4]. These authors investigated the solubility of water in the melt of the same granite used by Goranson. According to the brief abstract of their report at the Annual Geological Meeting at St. Louis, they also obtained a much lower figure. The general relationship of the three sets of data on the solubility of water in granitic melts is shown in the diagram of Fig. 5. Pointing out that the lower value for the solubility of water in granitic melt is geologically significant, Jahns and Burnham draw attention to the need for revision of the thermodynamic

Table 2

Results of Experiments on the Determination of Water in Quenched Melts Obtained After Melting Basalt and Granite in the Presence of Water at T = 900°C and P = 3000 kg/cm²

Weight of sample, g.	Increase in weight of Pregl tubes, g	Water content in the melt, %		Average water content in the melt, %
Basalt, first series (heated to 900°C)				
0,2683	0,0076		2,83	3,24
0,3439	0,0130		3,78	
0,3057	0,0107		3,50	
0,2368	0,0066		2,78	
0,2199	0,0073		2,32	
Second series (heated to 1000°C; held at 1000°C for one hour and at 900°C, for 2-1/2 hours)				
0,3518	0,0130		3,69	3,60
0,1785	0,0064	3,59	3,36	
0,2937	0,0092	3,13		
0,2576	0,0084		3,26	
0,2055	0,0080	3,89	3,86	
0,2964	0,0114	3,84		
0,3040	0,0117		3,84	
Granite				
0,1790	0,0124	6,92	6,60	6,68
0,3784	0,0238	6,28		
0,2643	0,0178	6,73	6,76	
0,3710	0,0252	6,79		

Note: Comma represents decimal point.

conclusions based on the older data. It should be added, however, that in spite of the discrepancy in the absolute values of solubility, the general shape of the solubility-pressure curves does not differ radically from the curve based on Goranson's data, judging by the values for the 900°C isotherm.

A comparison of the microscopic appearance of the cooled products resulting from melting of basalt and granite under the pressure, of a mixture of the volatiles from water and of the equivalent amount of hydrogen liberated during the experiment, clearly shows the greater crystallization capacity of basalt. This is well known in nature, where even under the

Table 3

Results of Experiment on the Determination of Water in Quenched Melts Obtained After Melting Basalt and Granite in the Presence of Water

T, °C	*p* kg/cm²	Weight of sample	Increase in weight of Pregl tubes, g	Water content in the melt, %	Average water content in the melt, %
			Basalt		
900	2000	0,2495	0,0065	2,60	2,60
		0,2283	0,0056	2,45	
		0,2666	0,0073	2,74	
900	1000	0,2328	0,0056	2,41	2,41
1000	3000	0,2281	0,0120	5,39	5,38
		0,1807	0,0097	5,36	
1000	2000	0,2849	0,0094	3,30	3,30
			Granite		
900	2800	0,2103	0,0136	6,47	6,47
900	2000	0,2145	0,0115	5,36	5,30
		0,3217	0,0169	5,25	
900	1000	0,3081	0,0086	2,79	2,79
1000	3000	0,2336	0,0132	5,36	5,36
1000	2000	0,2723	0,0128	4,70	4,70

Note: Comma represents decimal point.

usually low water vapor pressures under surface conditions the lower parts of basaltic flows exhibit holocrystalline texture. Increased pressure in the presence of volatiles enhances this capacity.

The usual microscopic appearance of cooled granitic melts is that of a homogeneous colorless field of locally brown glass with *N* = (1.486 – 1.501) $\pm$ 0.002 traversed by a network of cracks containing a few relicts of quartz or of altered biotite and newly formed hematite. A typical picture of granitic glass is shown in Fig. 6.

Unlike the granitic melt, the basaltic melt cooled under identical conditions looks like a well crystallized material (Fig. 7). The groundmass of the thin section consists of glass and hornblende with the glass being slightly predominant. The original basaltic glass with *N* > (1.507 – 1.510) $\pm$ 0.002 has become more siliceous. The composition of the new glass is fairly homogeneous, judging by the uniformity of the refractive index, *N* = 1.496 $\pm$ 0.002 in the different parts of the sample. Hornblende is somewhat subordinate to glass and occurs in green aggregates with noticeable pleochroism. The mineral is biaxial negative, with $c \wedge Z > 20°$, $N_g = 1.698 \pm 0.002$ and $N_p = 1.663 \pm 0.002$.

The relicts are represented mainly by fragments of pyroxene phenocrysts with only very slight signs of decomposition manifested by an

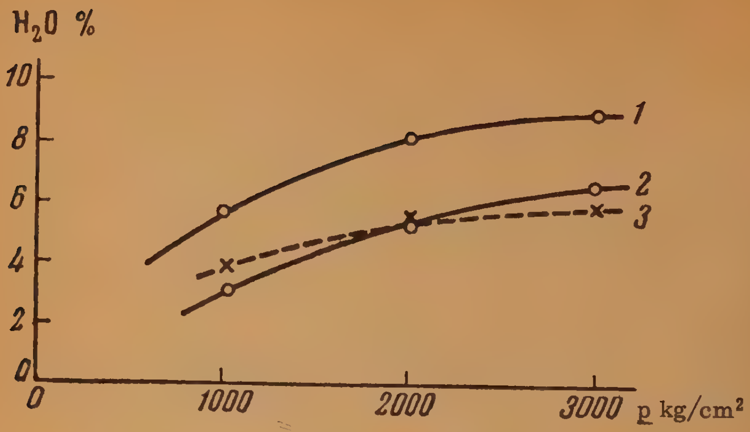

Fig. 5. Solubility of water in granitic melts according to the data of different investigators

1 -- Goranson's data for 900°C isotherm, 2 -- the authors' data for the same isotherm, 3 -- Jahns and Burnham's data, sample heated 20-30°C above the liquidus temperature

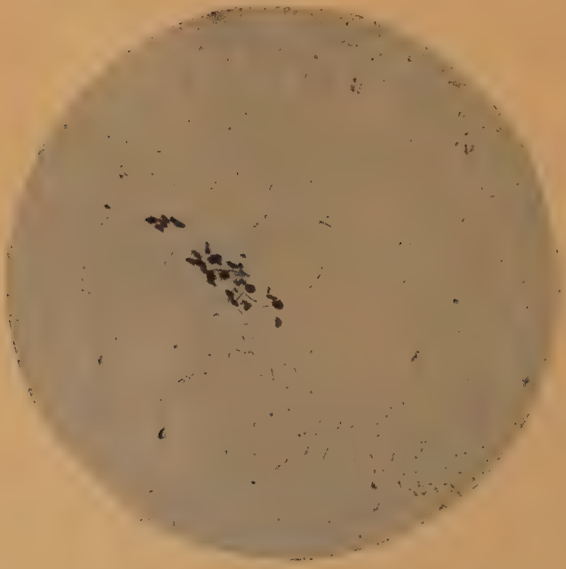

Fig. 6. General view of granitic melt under the microscope after experiment. Light-gray glass and segregations of hematite (x 100)

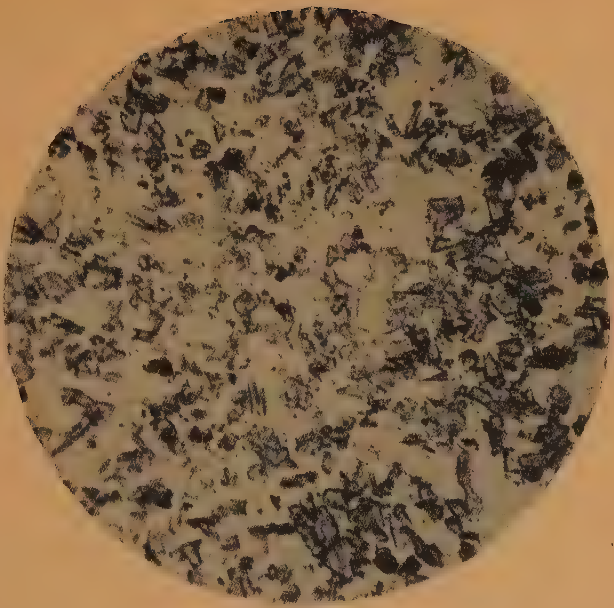

Fig. 7. General View of basaltic melt after experiment.
Glass and hornblende (x 100)

largement of cleavage cracks. Only the larger olivine grains occur as licts and they are often rimmed with replacing green hornblende (Fig. 8).

The pyroxene appears to be more stable, as was noticed by Winckler [5] his work on the alteration of olivine basalt at $\underline{T}$ = 740–640°C and under e pressure of 2000 bars in the presence of water. At 1000°C the pyroxene enocrysts become strongly replaced by hornblende. The newly formed rnblende in the groundmass, in this case, occurs in aggregates of smaller ains and as numerous green needles.

The relationship between the basaltic and granitic melts and the volatiles, ater and hydrogen, determines the form of occurrence of iron oxides. fter cooling, the granitic melts are characterized by hematite, the basalc melts by magnetite.

Although the basaltic melt dissolves less water than the granitic, the mount of dissolved water is sufficient to give rise under favorable geologil conditions to the various derivatives of basaltic magma.

In the natural basalt extruded to the surface, the water content is neglible, 0.06%, while the basaltic melt at 900°C and pressure of 3000 kg/cm^2 ay contain up to 3.6% of water. If it is assumed that before extrusion on e surface the melt was saturated with water, than its loss on extrusion is nsiderable. Each 10 m^3 of extruded basaltic magma may liberate up to e ton of water.

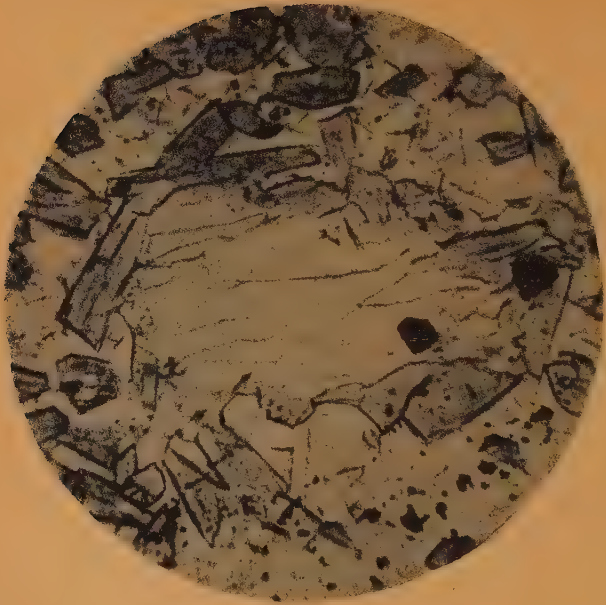

Fig. 8. Olivine with hornblende replacement rim (x 100)

During the movement of the magma towards the surface, the excess water may separate at once or periodically, depending on the physico-chemical conditions, governed to a considerable degree by the general geological setting. This separation of the volatile phase in some cases may be the cause of explosive activity, especially during the crystallization of the melt.

The basaltic magma, as it rises from the depths where temperature and pressure approximate 900°C and 300 kg/cm^2, respectively, must be pictured as a relatively mobile melt with crystals of pyroxene and olivine floating in it. It may be expected that under a favorable combination of geological conditions there will occur a separation of the crystallized fraction of ultrabasic composition and the more acid melt.

The data cited show that solubility of water in basaltic melt at 900°C and 3000 kg/cm^2 pressure is half the solubility of water in granitic melt. This confirms the opinion of many authors based on the geological data and the experimental data for individual systems that the water content in basaltic magma is low. This is the opinion of D. C. Belyankin, A. S. Ginzberg, T. Phemister, J. Gilluly, N. Bowen and many others [6–10].

The data given above show that at $T = 900°C$ and $P = 3000$ kg/cm^2 the basaltic melt dissolves 3.2 – 3.6% of water.

It can be seen from Fig. 9, however, that the great difference in the solubility of water in the two melts should not persist in the region of

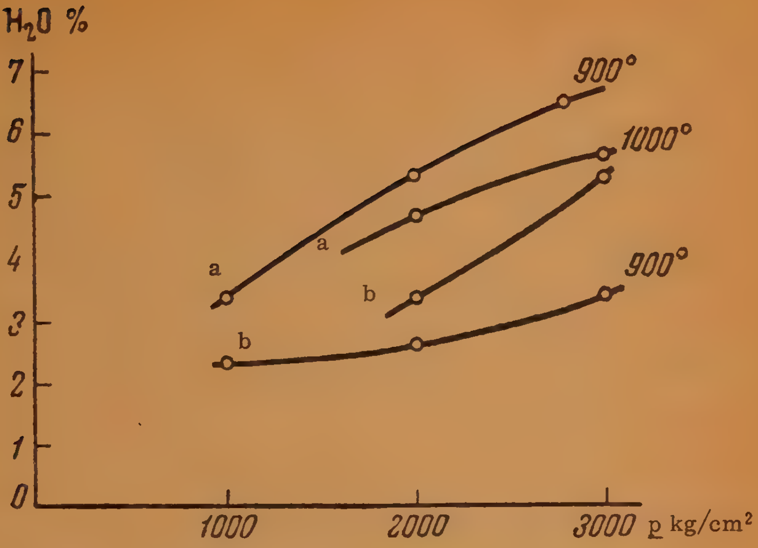

Fig. 9. Solubility curves of water at 900°C and 1000°C in granitic (a) and basaltic (b) melts at different water vapor pressures

temperatures above 900°C. Even at 1000°C the solubilities of water in granitic and basaltic melts approach each other. The possibility is not excluded that in a nearby high temperature region the two melts, in spite of their different chemical composition, will dissolve equal amounts of water. Further investigations are needed to clarify the relation between the silicate melt and the volatiles in this region.

In all experiments conducted under sufficient vapor pressure and in the presence of an equivalent amount of hydrogen, hornblende formed in the quenched melt. It is usually absent from the basic lavas extruded on the surface. These two phenomena reflect a number of peculiarities of the conditions existing during extrusion.

The absence of hornblende from extruded basalt indicates low water vapor pressure, lower than that required for the stability of hornblende, and a sufficiently high temperature of extrusion, for otherwise hornblende would occur among the intratelluric phenocrysts. But hornblende is usually absent from the hypabyssal basic rocks, such as diabase, and this may be considered as an indication of low water content in the primary basaltic magma itself. Moreover, the absolute water content established by experiment at pressures up to 3000 kg/cm² must, of course, be regarded as the maximum possible but not necessarily the usual content.

Summary

1. The solubility of water in the basaltic melt at 900°C and the pressure

of 3000 kg/cm^2 is about half of the solubility of water in the granitic melt under the same conditions. In the former, it is 3.2 - 3.6%, and in the latter, 6.8%.

2. At 1000°C and under the same pressure, the difference in the solubility of water in the two melts diminishes. The basaltic melt dissolves 5.38% of water and the granitic melt, 5.65%. This suggests the possibility that in a nearby high temperature region the two melts may dissolve the same amount of water in spite of the difference in their chemical composition.

3. The presence of hornblende in the quenched basaltic melts and the usual absence of it from the natural basalts and diabases may be regarded as an indication of low water content in the primary magma.

4. Basaltic magma rising from the depths where the temperature is 900°C and pressure 3000 kg/cm^2 may be pictured as a very mobile melt with pyroxene and olivine crystals floating in it.

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ON THE POST-PRECAMBRIAN GEOCHEMICAL HISTORY OF THE ATMOSPHERE AND HYDROSPHERE

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As a result of the studies begun 25 years ago by V. M. Goldschmidt [13] and continued in the post-war years in the USSR, the USA and elsewhere by W. Rubey, H. Urey and others, the basic concepts of quantitative geochemistry have been worked out which have advanced considerably our knowledge of the evolution of the chemical composition of the atmosphere and the ocean [6-8, 18, 30, 31, 39-42, etc.]. It has been proved that the principal cations in sea water (Na, K, Mg, Ca, Sr and others) and the elements of the sedimentary rocks (Si, Al, Fe, Ca, Mg, Na, K, Mn and others) were derived in the past from the weathering of the ancient rocks, while the water of the oceans and the principal anions contained in it (Cl, SO_4, CO_2, F, B and others), a considerable part of the atmospheric gases (N_2, CO_2 etc.) and the same components locked in the sedimentary rocks must have come from a different source. Calculations of the amount of these components in the present-day hydrosphere and atmosphere and in the ancient sedimentary rocks show that it is much greater than could have been produced by weathering. These materials, appropriately named the "excess" volatiles by Rubey, have been brought to the earth's surface from its depths by volcanic and intrusive activity throughout the geologic history of the planet. A well documented hypothesis has been advanced to the effect that the "excess" volatiles were derived primarily from the degassing of the earth's mantle, effected by various deep-seated processes [8, 17, 31 etc.]. One of the variants of this hypothesis, the most plausible in the author's opinion, was proposed by A. P. Vinogradov and is based on the concept of zonal melting of the mantle by radiogenic heat. Experimental work shows that such zonal melting would provide quantitatively for the simultaneous formation of the residual material of the mantle (dunite), the crust, the hydrosphere and the atmosphere [8, 9].

Scientists differ in their views on the duration and intensity of liberation of the volatiles from the depths of the earth during the geologic history. Some believe that the rise of the main mass of volatiles to the surface ended rather quickly, during the first hundreds of millions of years of the planet's life, and after that the process died out spasmodically in response to the general tectonic rhythm of the earth [8, 9]. Others believe that the degassing proceeded gradually at an approximately uniform rate. The most consistent adherent to this concept is Rubey, who bases his argument on computations and numerous facts from various fields of knowledge [30, 31].

If Rubey's view is accepted that the amount of CO_2 in the atmosphere and ocean remained relatively constant during the greater part of geologic time and the "excess" volatiles accumulated gradually, then the conclusion is inevitable that, in order for these conditions to persist, in the system atmosphere-ocean there must have been a continuously active mechanism of removal and fixation of carbon dioxide introduced from the depths of the earth by volcanic activity in the broad sense of the term.

The effect of this mechanism in the geologic past can be determined only by obtaining quantitative data on the variation in the intensity of volcanism during a sequence of epochs and periods and by measuring the amount of carbon dioxide locked in the sedimentary rocks during the same segments of time. Until recently this problem seemed unsolvable.

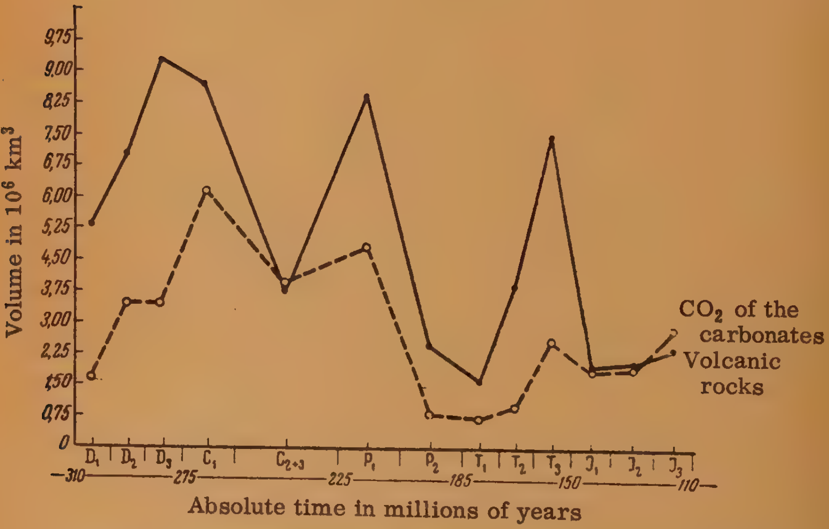

Fig. 1. Relation between the volumes of subaqueous and subaerial volcanic extrusions and the volumes of CO_2 locked in the carbonate rocks of the present day continents

Note: Comma represents decimal point.

Recently the necessary data were obtained by the author and V. E. Khaimov in the course of compiling lithological-paleogeographic maps of the continents on a 1:25,000,000 scale. During the ten years of work on the projected series of maps for all of the post-Proterozoic epochs, maps of the Devonian, Carboniferous, Permian, Triassic and Jurassic systems [24-28] were completed. They show for each epoch the distribution of the different types of rocks and their associations (rock units) and the variations in their thicknesses in the platform and geosynclinal areas lying within the boundaries of the modern continents. By means of the volumetric method developed earlier by the author [19, 20, 21], the areas of distribution and the approximate volumes of the principal sedimentary and volcanic rocks were measured. The results of these measurements in simplified diagrammatic form are given in the table. A graph constructed on the basis of these data shows the variation in time of the volume of subaqueous and subaerial volcanic extrusions and of the volume of carbon dioxide locked in the carbonate rocks (Fig. 1). The juxtaposition of the curves on the graph presents in a laconic quantitative form the effect of the mechanism mentioned above.

It is known that the composition of the gases emanating from volcanoes and fumaroles is very similar to the composition of the "excess" volatiles (Rubey [30]). According to the data of E. Allen and E. Zies, J. Verhoogen, A. Rittmann, K. Sapper, E. Shepherd, A. Ellis, L. S. Selivanov, S. I. Naboko and others [1, 32, 37, 46], the amount of carbon dioxide, water and other components emitted by volcanoes is proportional in the first rough approximation to the volume of the lavas in which these volatiles were dissolved. If this is true, then it may be tentatively assumed that the curve representing the volume of subaqueous and subaerial volcanic effusions (Fig. 1) is a measure of the intensity of separation of the "excess" volatiles (including CO_2) from the molten (effusive) volcanic products into the system atmosphere-hydrosphere for each epoch of the investigated segment of time (D_1 - J_3). This is only a first approximation, for the curve shows the volume of extrusions not for the entire earth's surface but only for about 29.2% of it lying at present within the continents and large islands. The volume of the corresponding extrusions over the area of the present-day oceans remains unknown. It cannot be measured today, but in view of the more or less contemporaneous manifestation of volcanism on the different continents, it may be supposed with sufficient plausibility that the intensity of volcanism in the oceans was more or less similar to that on the continents. This is the more probable, for lately a number of geologists have expressed the opinion that the Atlantic, Indian and Arctic oceans are relatively young (Mesozoic) and were formed as a result of large downwarpings of the earth's crust at the sites of ancient continents and inland seas [3]. In particular, these concepts apply to the southern part of the Atlantic and the entire Indian ocean, which, it is supposed, were sites of a single complex of continents and inland seas during the Middle and Upper Paleozoic and the very beginning of the Mesozoic. This complex--Gondwanaland--comprised, besides the now submerged areas, the modern continents of South America, Africa, Australia, Antarctica and the peninsula of India. It may be supposed that, in the now submerged part of Gondwanaland, volcanic activity was synchronous and comparable in intensity with the volcanism on its surviving parts.

The large-scale subsidences of the earth's crust were accompanied by the filling of the newly formed depressions with oceanic waters. The absence of deep water oceanic sediments on the modern continents and the unchanged regime of marine transgression and regression within their boundaries after the formation of the ocean basins leads to the conclusion that water was continually added to the growing oceanic reservoir during the course of geologic time. Evidently during this process the salinity of the oceans underwent continuous change by the introduction of metallic ions from the continents (weathering) and of anions from volcanic emanations.

The parallelism of the curves of Fig. 1 indicates that the volcanic carbon dioxide added to the atmosphere and ocean was almost at once extracted from these reservoirs and locked in the carbonate rocks deposited on the bottom of the shallow geosynclinal and cratonic seas. Theoretical considerations provide an adequate basis for assuming that carbon dioxide was extracted from the atmosphere and ocean quite thoroughly and more or less simultaneously with its introduction from the deep sources. The deviations from this rule must have been rare and short lived, for otherwise there would have been a considerable increase in the partial pressure of carbon dioxide in the atmosphere. As a result of this, the previously deposited limestones would have been dissolved and further deposition of carbonate rocks would have ceased. It is this mechanism that prevented the secretion of calcareous skeletons by the invertebrates in the early Precambrian [5]. The presence of carbonate rocks in all post-Precambrian epochs shows that even if the partial pressure of CO_2 in the atmosphere increased at times, the increase was short lived and the dynamic equilibrium between addition and fixation of carbon dioxide was soon reestablished.

At present there is no direct evidence of the presence of Paleozoic calcareous deposits on the ocean bottom. The author believes that the accumulation of carbonate sediments on the ocean bottom during the Paleozoic was insignificant. If, as is generally believed, the partial CO_2 pressure was relatively higher then than now and equilibrium existed between the carbon dioxide of the atmosphere and of the hydrosphere, no precipitation of carbonates could have occurred on a large scale, except in small land-locked seas where evaporation could have caused the oversaturation required for precipitation of $CaCO_3$. It should be added that the absence of intensive precipitation of carbonates in the ancient oceans is indicated also by the excess of calcium in the Paleozoic inland sea deposits. The main mass of calcium transported from the continents was evidently precipitated in the inland seas before reaching the oceans.

One more important deduction can be made from the comparison of the data in the Table and examination of the curves of Fig. 1. The addition of the volatiles to the atmosphere and the accumulation of carbonate rocks did not occur at a uniform rate throughout geologic time, but with pronounced periodical variations as indicated by the peaks on the graphs. During the investigated segments of time, the epochs of intensive volcanism and great accumulation of carbonates (D_3-C_1, P_1, T_3, J_3) alternated with periods of less intensive volcanism and proportionately diminished deposition of carbonate sediments (D_1, C_{2-3}, P_2-T_2, J_{1-2}). These fluctuations are in good agreement with the general periodicity of marine transgressions and regressions (Fig. 2).

A comparison of Figs. 1 and 2 reveals an unquestionable direct relation between the area covered by the sea and the mass of accumulated carbonate rocks. The amount of carbonate sediments increased as the inland seas spread, and diminished proportionately as they shrank.

Thus, it must be concluded that the periodic fluctuations in the amount of carbonate sediments were governed by the corresponding periodic changes in the intensity of the interrelated volcanic and tectonic (epeirogenic) processes. The former provided the quantity of carbon dioxide needed for the accumulation of the carbonates; the latter determined the area of the inland seas, i. e. the area of the medium favorable for the accumulation of the carbonates. From these relationships the basic law of

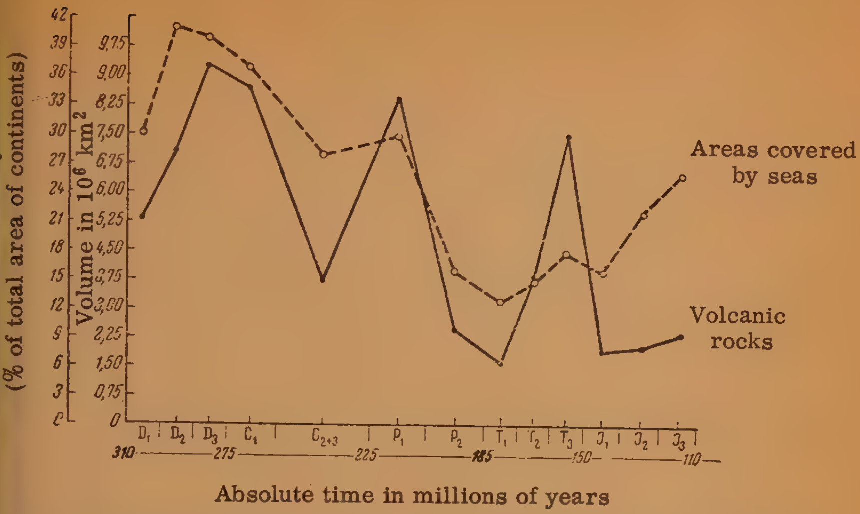

Fig. 2. Relation between volumes of volcanic extrusions and marine transgressions and regressions on the area of the present day continents

Note: Comma represents decimal point.

ccumulation of carbonates may be formulated: the quantity of carbonate ediments deposited in a given post-Precambrian epoch was directly proortional to the intensity of volcanism and to the area of distribution of land seas.

According to Rubey's data [30, 31], 92 • 10^{15} tons of CO_2 are locked in e sedimentary rocks of the earth. The author's measurements (Table) how that the Devonian, Permian, Triassic and Jurassic carbonate rocks lone contain 95 • 10^{15} tons of CO_2. If the carbon dioxide locked in the roterozoic, Lower Paleozoic, Cretaceous and Cenozoic limestones, and the carbonate admixtures of the argillaceous and arenaceous rocks, as ell as the organic carbon disseminated through the sediments, are taken to account, a figure much larger than that given by Rubey is obtained. ubey's figure is obviously too low and requires revision. At the same me, one cannot disagree with Rubey's statement that the main mass of rbonate rocks was deposited during the Paleozoic and that Precambrian rbonate rocks constitute but a small percentage of the total carbonate posits. This is a fact of primary importance, but an exact interpretation it is very difficult. One is naturally tempted to conclude that the intenity of liberation of the "excess" volatiles (including CO_2), and of the asciated process of fixation of CO_2, not only did not diminish after the recambrian, but even increased substantially during the Paleozoic. However, certain corrections are needed, for it is not known what part of the xcess" volatiles brought to the surface by volcanic activity was juvenile, rectly related to the degassing of the earth's mantle, and what part was cycled as a result of remelting by the magma of the earlier limestones d the clastic rocks containing carbonates and disseminated organic carn [4]. Finally, although carbonate rocks are very scarce in the Archean, Areas of Distribution and Volumes of Different Rock Types on Platforms, Geosynclines and Continents as a Whole in Devonian, Carboniferous, Permian, Triassic and Jurassic Periods

System or series	Platforms, geosynclines, continents	Areas in million km²		Areas of accumulation in % of the total area of continents	Areas covered by seas in % of the total area of continents
		areas of erosion	areas of accumulation		
Lower Devonian (D_1)	Platforms	61,1	19,9	25	17
	Geosynclines	20,3	30,3	60	51
	Continents	81,4	50,2	38	30
Middle Devonian (D_2)	Platforms	58,0	23,1	28	20
	Geosynclines	11,3	40,3	78	73
	Continents	69,3	63,4	48	41
Upper Devonian (D_3)	Platforms	60,3	20,5	25	19
	Geosynclines	10,8	40,7	79	74
	Continents	71,1	61,2	46	40
Lower Carboniferous (C_1)	Platforms	68,1	16,0	19	16
	Geosynclines	9,8	37,6	79	74
	Continents	77,9	53,6	41	37
Middle and Upper Carboniferous (C_{2+3})	Platforms	63,3	26,9	29	13
	Geosynclines	12,9	29,5	70	61
	Continents	76,2	56,4	42	28
Lower Permian (P_1)	Platforms	64,6	22,8	26	13
	Geosynclines	15,2	29,0	66	57
	Continents	79,8	51,8	39	30
Upper Permian (P)	Platforms	77,1	13,6	15	5
	Geosynclines	19,8	20,5	51	41
	Continents	96,9	34,1	26	16
Lower Triassic (T_1)	Platforms	91,5	12,1	12	4
	Geosynclines	15,0	14,9	50	45
	Continents	106,5	27,0	20	13
Middle Triassic (T_2)	Platforms	95,7	7,0	7	5
	Geosynclines	14,5	16,4	53	48
	Continents	110,2	23,4	17	15
Upper Triassic (T_3)	Platforms	80,3	22,3	22	5
	Geosynclines	7,0	22,9	76	62
	Continents	87,3	45,2	34	18
Lower Jurassic (J_1)	Platforms	88,1	18,4	17	7
	Geosynclines	7,3	17,6	71	65
	Continents	95,4	36,0	27	16
Middle Jurassic (J_2)	Platforms	77,3	29,6	28	12
	Geosynclines	7,6	17,9	70	62
	Continents	84,9	47,5	36	22
Upper Jurassic (J_3)	Platforms	76,0	31,2	29	16
	Geosynclines	6,0	18,1	75	69
	Continents	82,0	49,3	37	26
Total for the L. Devonian to U. Jurassic interval ($D_1 - J_3$)					

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* This quantity of CO_2 is 95 · 10^{15} tons.

Note: Comma represents decimal point.

Table (Continued)

Volumes in million km³							
continental clastics	marine clastics	lagoonal-saline rocks	marine and lagoonal carbonate rocks	CO_2 in the carbonate rocks	volcanic rocks on land	sub-aqueous volcanics	total volume of deposits
2,76 1,39 4,15	3,45 10,47 13,92	0,02 0,00 0,02	0,21 3,54 3,75	0,09 1,56 1,65	0,00 0,95 0,95	0,00 4,35 4,35	6,44 20,70 27,14
1,26 1,58 2,84	2,63 10,52 13,15	0,15 0,03 0,18	1,19 6,65 7,84	0,52 2,93 3,45	0,00 1,05 1,05	0,00 7,00 7,00	5,23 26,83 32,06
1,64 2,06 3,70	2,10 8,74 10,84	0,12 0,00 0,12	2,14 5,67 7,81	0,94 2,50 3,44	0,00 0,69 0,69	0,00 8,64 8,64	6,00 25,80 31,80
0,91 2,16 3,07	1,36 6,37 7,73	0,09 0,03 0,12	2,41 11,55 13,96	1,06 5,09 6,15	0,00 0,35 0,35	0,00 8,35 8,35	4,77 28,81 33,58
4,77 4,59 9,36	2,08 7,85 9,93	0,02 0,00 0,02	1,89 7,16 9,05	0,83 3,15 3,98	0,00 0,26 0,26	0,00 3,52 3,52	8,76 23,38 32,14
3,42 2,28 5,70	1,98 5,16 6,44	0,61 0,22 0,83	2,24 8,88 11,12	0,99 3,91 4,90	0,00 1,13 1,13	0,00 7,36 7,36	7,55 25,03 32,58
3,79 3,43 7,22	0,53 5,73 6,26	0,08 0,08 0,16	0,39 1,55 1,94	0,17 0,68 0,85	0,00 0,17 0,17	0,00 2,33 2,33	4,79 13,29 18,08
3,06 0,74 3,80	0,76 3,39 4,15	0,05 0,00 0,05	0,55 1,12 1,67	0,24 0,49 0,73	0,39 0,04 0,43	0,00 1,21 1,21	4,81 6,50 11,31
0,59 0,93 1,52	0,60 4,51 5,11	0,002 0,01 0,012	0,58 1,86 2,44	0,25 0,82 1,07	0,08 0,30 0,38	0,00 3,55 3,55	1,85 11,16 13,01
6,86 3,97 10,83	0,80 9,45 10,25	0,13 0,002 0,132	0,59 4,43 5,02	0,26 1,95 2,21	2,32 0,76 3,08	0,00 4,45 4,45	10,70 23,06 33,76
4,53 0,73 5,26	0,92 8,53 9,45	0,01 0,001 0,011	1,32 3,02 4,34	0,58 1,33 1,91	0,001 0,13 0,131	0,00 1,84 1,84	6,78 14,25 21,03
4,07 0,94 5,01	1,89 8,95 10,84	0,01 0,002 0,012	1,81 2,58 4,39	0,80 1,14 1,94	0,02 0,03 0,05	0,00 2,00 2,00	7,80 14,50 22,30
2,83 1,37 4,20	2,86 8,82 11,68	0,34 0,23 0,57	3,00 3,43 6,43	1,32 1,51 1,83	0,30 0,60 0,90	0,00 1,44 1,44	9,33 15,89 25,22
40,49 26,17 66,66	21,26 98,49 119,75	1,632 0,705 2,237	18,32 61,44 79,76	8,05 26,06 34,11*	3,11 6,46 9,57	0,00 56,04 56,04	84,81 249,20 334,01

this is not a proof that they were not formed at that on a large scale.

As a result of very intensive regional metamorphism, many carbonate rocks were changed into metamorphic rocks rich in calcium-magnesium silicates and aluminosilicates (diopside, garnets, etc.).

These considerations are confirmed by the data of tectonics and historical geology. The periodic variation in the intensity of volcanism and related processes occurred against the background of general diminution of the area of volcanic activity. Effusive activity, as is known, is almost restricted to the geosynclines, and except during the Upper Triassic, has been insignificant on the platforms. In post-Cambrian time, the growth of the platforms at the expense of the geosynclines is traceable from one tectonic cycle to the next [2, 34, 43, 45]. It is to be expected, therefore, that the total absolute intensity of intrusive and extrusive igneous activity on the earth as a whole diminished with the growth of the platforms. This is probably true, but quantitative data confirming this hypothesis are available only for the segment of time investigated by the author (D_1–J_3), i. e. for the Hercynian and the first half of the Alpine tectonic cycles (see Fig. 1 and Table).

The end of the Precambrian is the starting point of our investigation. By this time, green plants attained a complete monopoly in the synthesis of organic matter [16]. Large amounts of juvenile carbon dioxide were continually withdrawn from the atmosphere and the ocean, and free oxygen was liberated from water by photosynthetic fixation of carbon by the plants. The oxygen was added to the atmosphere and the ocean and a part of it was expended in the oxidation of organic matter, iron, manganese, sulfur and other multivalent elements present in the rocks, sediments and waters. Only a small part of the organic carbon formed stable compounds immune to bacterial action [33], and these compounds were buried in the sedimentary strata forming the so-called dispersed organic matter and accumulations of caustobioliths (coals, petroleum, natural gas, etc.). The mass of dispersed organic carbon (C_{org}) is more than 1000 times as great as the amount of it in the caustobioliths. At the same time, preliminary computations show that the mass of C_{org} is 2.7 - 3.0 times less than the mass of carbon locked in the carbonate rocks. This is such a large quantity that it cannot be neglected, and deserves special consideration.

For lack of data, the author had to forego direct determination of the mass of organic carbon locked in the sedimentary rocks of the continents and to find a different method of investigation. Using 26,000 samples selected from cores of numerous holes drilled in the sedimentary cover of the Russian platform at many localities, he made 1000 representative average samples of the argillaceous, carbonate and arenaceous strats representing all geological systems and series (and sometimes stages) from the Upper Proterozoic (Sinian) to the Quaternary, the deposits of petroliferous and nonpetroliferous provinces of the different tectonic zones of the Russian platform and different facies and geochemical environments of sedimentation. These samples were subjected to careful chemical analysis [10-12, 29] for organic carbon and many other components [23]. The results of the determinations were processed statistically and compared with P. D. Trask and H. W. Patnode's data [38] on the distribution of C_{org} in the sedimentary complexes of corresponding ages in the United States (Fig. 3). In comparing the graphs, attention is attracted by the similar alternation of periods of enrichment and impoverishment in dispersed organic matter in the two regions, so distant from each other and lying on different continents and in different hemispheres. Such similarity can hardly be accidental;

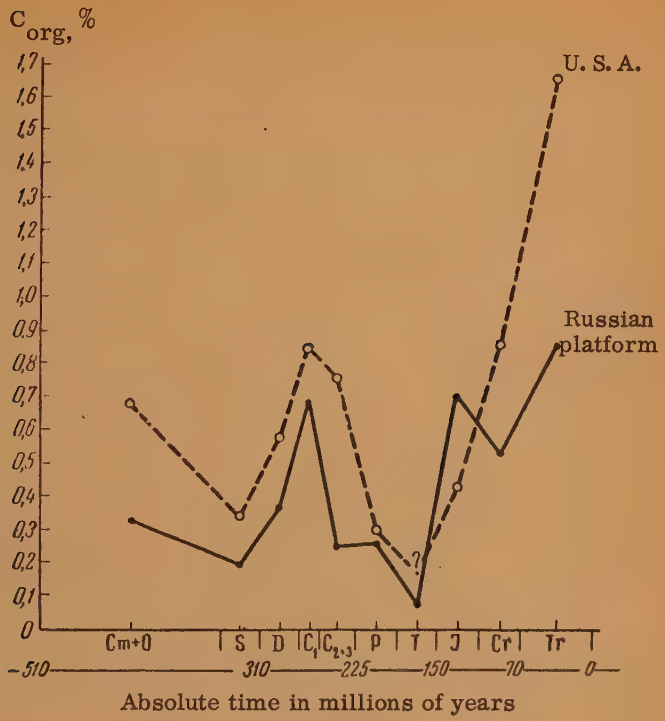

Fig. 3. Variation in the average content of organic (C_{org}) in the sedimentary rocks of the Russian platform and the United States of America

Russian platform -- 1024 analyses of average samples prepared from 23052 samples (after A. B. Ronov); U. S. A. -- 7052 analyses of individual samples (after Trask and Patnode)

it suggests a tendency common for the entire earth towards periodical intensification and weakening of organic activity, whose traces are recorded in the sedimentary strata. The alternation of maxima and minima in the development of life was intimately related to changes in the geographical and climatic environments on the earth's surface, but, in the final analysis, was evidently governed by the same factors which determined the deposition of carbonate rocks. It is impossible to check this hypothesis rigorously, for there are no data on the distribution of C_{org} in the deposits of each of the Paleozoic and Mesozoic epochs in the United States. A comparison of the curves of Fig. 1 with the average figures for the Russian platform [23] shows a general synchronism and an identical trend in the variation of the amount of buried C_{org} and of the volume of volcanic extrusions. An exception to this is the Lower Permian epoch, which shows an opposite tendency (a diminished C_{org} content in spite of the general intensification of volcanic activity).

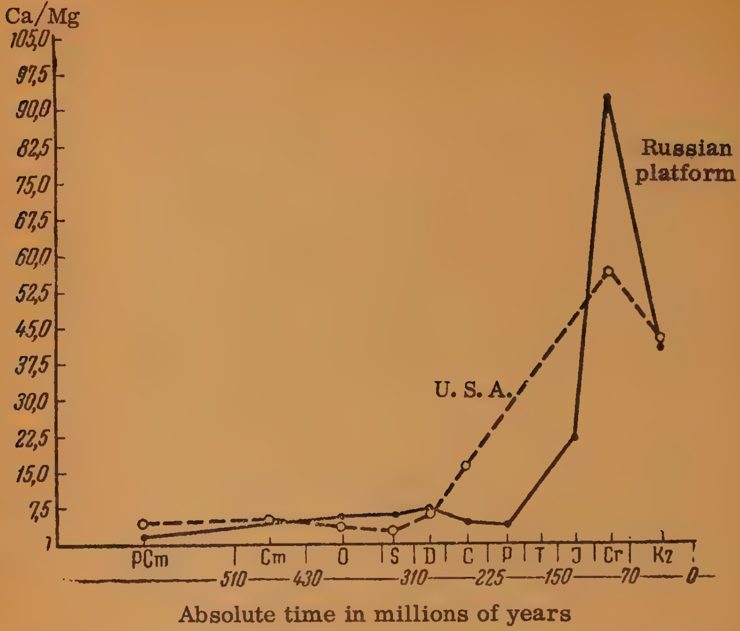

Fig. 4. Variation in the Ca/Mg ratio in time in the carbonate rocks of the Russian platform (after A. P. Vinogradov, A. B. Ronov and V. M. Ratynskii) and of North America (after R. Daly)

Russian platform -- 282 analyses of average samples prepared from 10029 samples; North America -- 853 analyses of individual samples

In view of the similarity in the distribution of C_{org} in the rocks of the United States and the Russian platform for the entire geological periods (Fig. 3), it may be assumed that this similarity holds also for the shorter intervals of geologic time--epochs. If this is correct, it follows that not only the quantity of CO_2 in the carbonate rocks depends on the intensity of volcanism, but also the quantity of organic matter dispersed through the sedimentary strata and its concentration in the caustobioliths. So far, this is only an insufficiently documented guess requiring further verification.

One other very important question arises from the survey data: has the absolute amount of carbon dioxide in the atmosphere and the ocean changed during post-Precambrian time? This question can be answered only indirectly by using the data on the lithological and chemical composition of the sedimentary rocks of different geological ages. Especially interesting is the study of variation in the calcium-magnesium ratio in the carbonate rocks, which serves as a kind of indicator of the carbon dioxide regime in the system atmosphere-ocean.

Fifty years ago, Daly [14], in comparing a relatively small number of analyses of Paleozoic and Mesozic-Cenozoic carbonate rocks of the U. S. A., showed for the first time that the intensity of dolomitization has been decreasing throughout the earth's history. This was confirmed later by extensive analytical material for the rocks of the same ages on the Russian platform [10]. The dolomites, which were the dominant carbonate rocks in the Proterozoic, were gradually crowded out from the sedimentary sequences by limestones. A comparison of the curves of the Ca/Mg ratios in the carbonate rocks of the Russian platform and the U. S. A. shows that the evolution in the composition of the carbonate rocks on the two continents had the same trend (Fig. 4). Similar changes in the composition of the carbonate rocks are found on the Chinese platform. These combined data indicate a non-recurrent evolution of the carbonate rocks on the earth as a whole [10].

The comparative lithological-geochemical investigations of the ancient and modern carbonate rocks [35, 36], an investigation of the regularities in the variation of the chemical composition of these rocks in the ancient sedimentation basins [22] and experimental work on the formation of dolomite in sea water under high CO_2 pressure [15, 44] have brought together facts which indicate unequivocally that dolomitization was governed not only by the climatic conditions and the salinity of the waters in the basins but, first of all, by the much higher alkali reserves and the high CO_2 content in the water [36]. Examining the curves of Fig. 4 with these facts in mind, it may be asserted with sufficient certainty that against the background of dynamic equilibrium between the addition and fixation of carbon dioxide in the system atmosphere-ocean, the content of CO_2 underwent certain periodic variations in time, remaining relatively high until the end of the Paleozoic (mainly dolomites were deposited). During the Mesozoic era and especially in the Cretaceous period, the partial pressure of CO_2 became sharply reduced and the dominant role among the carbonates was assumed by calcium carbonate (limestones, chalk). It is appropriate to mention in this connection that it is precisely during the Upper Cretaceous and the Paleogene that the accumulation of the calcareous globigerina ooze began over the vast areas of the world ocean, which also points clearly to the diminution of the partial carbon dioxide pressure in the atmosphere.

Summary

The examined data show that in the system atmosphere-ocean, in the post-Precambrian geological periods the mechanism of removal and fixation of the abyssal (volcanic) carbon dioxide by the precipitation of the carbonates and by the photosynthetic fixation of carbon by green plants was continuously active. When viewed over considerable intervals of time equal in length to geological epochs, this mechanism appears to have been quite accurate. The quantity of the carbonate sediments deposited in this or that epoch was directly proportional to the intensity of volcanism and to the area covered by inland seas. Against the background of dynamic equilibrium between the addition and fixation of CO_2 in post-Precambrian time, the average partial pressure of carbon dioxide in the system atmosphere-ocean diminished. During the Paleozoic the decrease in P_{CO_2} was very slow but it accelerated sharply beginning with the Mesozoic. An indicator of this process is the change in the Ca/Mg ratio in the carbonate rocks with time.

In conclusion, the author thanks A. P. Vinogradov and A. I. Tugarinov for reading this paper in manuscript and for making a number of valuable suggestions which were incorporated in the final draft.

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PARAGENESES OF DARK MINERALS IN ALKALIC ROCKS AND A NEW EXPRESSION FOR THE AGPAITIC COEFFICIENT

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The significance of the ratio of sodium and potassium to aluminum in the analysis of parageneses of minerals in igneous rocks has been pointed out by many investigators (N. W. Ussing, V. M. Goldschmidt, A. E. Fersman, F. Yu. Loewinson-Lessing, A. N. Zavaritskii, V. V. Shcherbina, V. I. Gerasimovskii, V. S. Sobolev and others). The "agpaitic coefficient," i. e., the ratio of the molecular amounts of soda and potash to alumina $\left(\frac{Na_2O + K_2O}{Al_2O_3}\right)$, was generally accepted after V. M. Goldschmidt's work on mineral paragenesis. He proposed the division of rocks into agpaitic, in which this ratio is greater than one, and plumasitic, in which alumina is in excess of the alkalies and the ratio is less than one. The soundness of this kind of paragenetic analysis was demonstrated by Shcherbina on many examples [10].

In their studies of alkalic rocks, Fersman and Gerasimovskii used this ratio to subdivide nepheline syenites into agpaitic and miaskitic types [9, 1].

However, it was pointed out by Gerasimovskii that the "occurrence in the agpaitic nepheline syenites of minerals characteristic of miaskites shows that in the solution of geochemical and mineralogical problems of nepheline syenite intrusions, the agpaitic coefficient is not always reliable" [1]. This statement is true not only of the rare minerals of alkalic rocks (zircon, eudialyte and others) but of the common dark rock-forming minerals such as aegirine and alkalic amphiboles.

Thus, aegirine, a typical mineral of the agpaitic assemblage, appears in many plumasitic rocks with the value of the agpaitic coefficient greater than one (solvsbergite, Na-minette, some foyaites and urtites).

In Zavaritskii's system of numerical characteristics, [4] the agpaitic rocks are supposed to have parameters $\underline{c}$ and $\underline{n}'$ and is referred to the group of rocks with normal composition. Moreover, these parameters must be obtained by recalculating the complete chemical composition of the rock, which is not always possible and is time consuming.

These considerations suggest the desirability of deriving a coefficient which would contain the ratio of the alkalies to alumina and be convenient in calculations, and would distinguish sharply and accurately between the agpaitic and plumasitic assemblages.

The following coefficient is proposed here:

$$(Na)^{*} = \frac{Na}{Al - K} = \frac{Na}{\Delta Al}.$$

In this ratio, ΔAl represents the relative number of Al atoms remaining in the melt after a part of the Al has united with the available K atoms in one to one ratio, mainly in the K-Na feldspars. The tendency of potassium to form minerals from silicate melts earlier than any other cation was noted by Loewinson-Lessing: "Potassium has a stronger affinity for silica than sodium and the alkaline earths. Therefore, it always tends to form the most acid salts possible in a magma of a given acidity" [7]. Naturally, in the alkalic magmas undersaturated with silica the most "acid potassium salt" is the K-Na feldspar.

The other part of the Al (ΔAl) atoms will unite with Na in albite and nepheline in a 1:1 ratio. It may be assumed, therefore, that Al is distributed, first of all, among the alkalies in the alkali feldspars and feldspathoids. This is in agreement with Sobolev's opinion that there exists "... a definite order in the formation of the aluminosilicates with different cations which leads to definite sequences in the parageneses. The most active is the strongest base, K_2O, then comes Na_2O, and only the remainder of the aluminum enters into the calcium aluminosilicate" [8].

The $(Na) = \frac{Na}{\Delta Al}$ ratio itself will show, therefore, the amount of excess or deficiency of Na with respect to Al leading either to an agpaitic or to a plumasitic mineral association.

It is considered that the K-Na feldspars, albite and nepheline, are neither agpaitic nor plumasitic minerals, since in them the alkali-aluminum ratio is one to one. Theoretically, in a rock composed of these minerals only, the $\frac{Na}{\Delta Al}$ ratio must be one. The appearance of the minerals in which $Na:Al > 1$ must make the value of (Na) greater than one, just as the appearance of minerals with $Na:Al < 1$ (or minerals with $K:Al < 1$) must make the value of (Na) less than one. The value of the coefficient $(Na) = \frac{Na}{Al - K}$ has a direct bearing on the subdivision of rocks into the agpaitic and plumasitic.

Indeed, the agpaitic association is characterized by the appearance of dark minerals in which it is precisely Na that occupies the dominant or very important place in the cation group while Al is absent or subordinate (aegirine, alkalic soda amphiboles, lamprophyllite and other less common minerals). In the plumasitic association (or miaskitic in the case of nepheline syenites) the dark minerals are either free of Na or else Na plays a secondary role in them, and the dominant position is occupied by other cations, such as Ca^{2+}, Mg^{2+}, and Fe^{2+}. These dark minerals (micas, augite, common hornblende, etc.) sometimes have a considerable aluminum content. The older expression for the agpaitic coefficient showed only the ratio of the sum of the alkalies to Al, and did not reveal and emphasize the very important role of Na in relation to Al indicated by the (Na) coefficient. It will be shown, moreover, that the values of (Na) are more sensitive to the appearance of the various typical agpaitic or plumasitic minerals as compared with the values of the older agpaitic coefficient. The present paper reviews the more common types of alkalic rocks which, in addition to the different syenites, include alkalic gabbroids, urtite-ijolites and certain varieties of granites.

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*Na, Al and K are given in relative numbers of atoms for convenience and clarity. Calculations with molecular amounts can also be made.

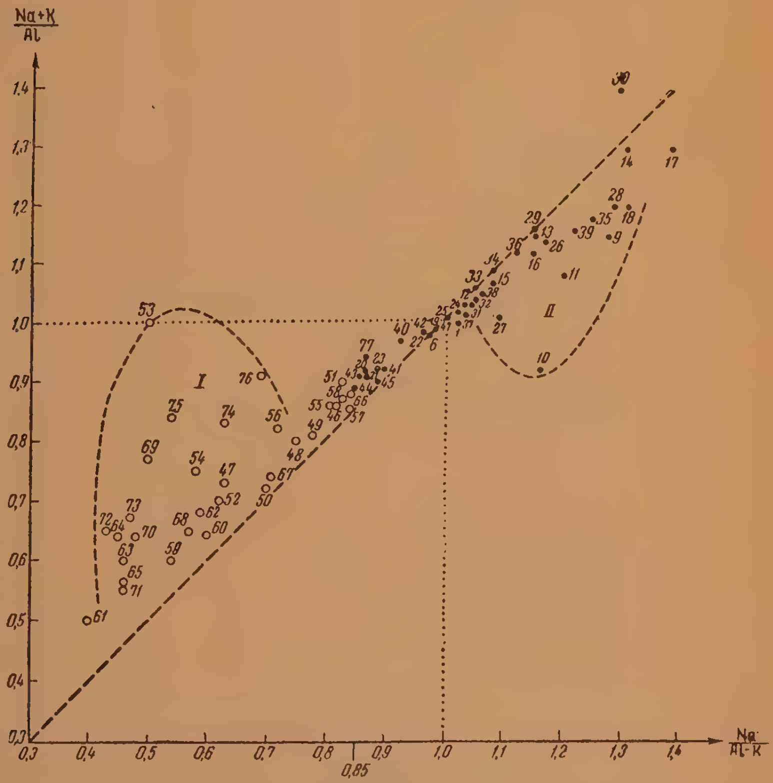

Fig. 1. Comparison of the $\frac{Na + K}{Al}$ and $\frac{Na}{Al - K}$ ratios for alkalic rocks. The names of the rocks are given in the Appendix under corresponding numbers.

● -- compositions with the agpaitic paragenesis of dark minerals (aegirine, riebeckite, arfvedsonite etc); o -- compositions with the plumasitic paragenesis of dark minerals (biotite, augite, common hornblende, magnetite)

Note: Comma represents decimal point.

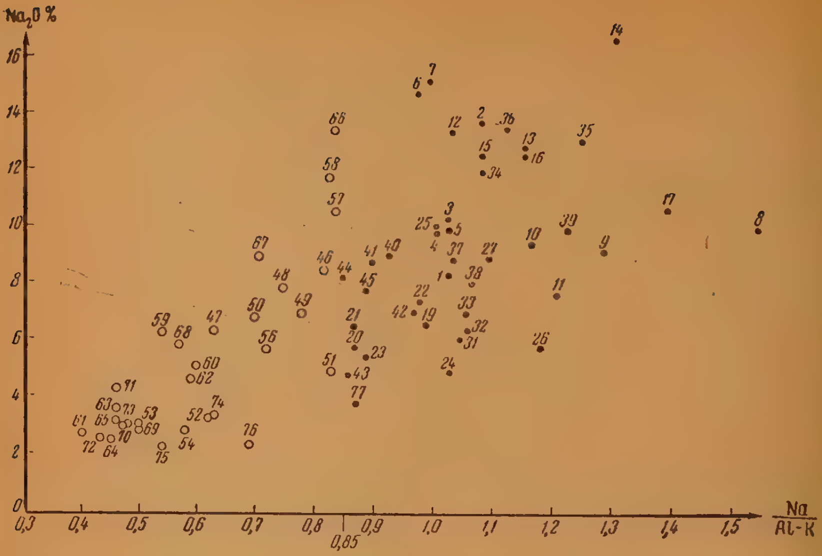

Fig. 2. Dependence of agpaitic and plumasitic associations of dark minerals in alkalic rocks on the Na_2O content (symbols as in Fig. 1)

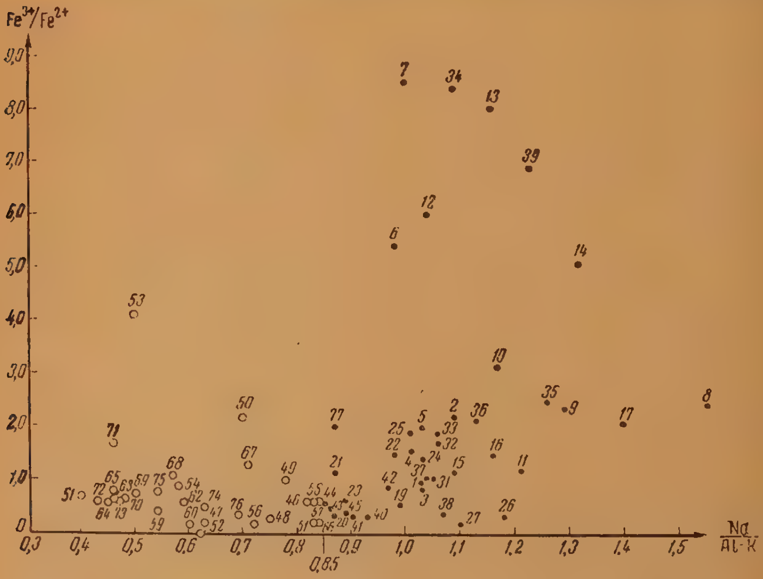

Fig. 3. Dependence of agpaitic and plumasitic associations of dark minerals in alkalic rocks on the Fe^{3+}/Fe^{2+} ratio (symbols as in Fig. 1)

Note: Comma represents decimal point.

Recalculation of 77 analyses given in the Appendix shows that the theoretical value of one of the agpaitic coefficient used in the analysis of parageneses is actually less than one. For the coefficient (Na) = $\frac{Na}{Al - K}$, it is 0.85 and for the old ratio, $\frac{Na + K}{Al}$, it is about 0.9 (see Appendix and Figs. 1, 2 and 3).

The decrease of the agpaitic coefficient to less than one may be due to the fact that in the actual rock-forming alkali feldspars and nepheline there is a certain excess of Al in relation to the alkalies which causes a deviation of the (Na, K):Al ratio in these minerals towards an excess of alumina.

The possible cause of the slight excess of Al in these minerals is the statistical distribution of aluminum, the second most important component of rocks after Si, in the (Si, Al) tetrahedra. The necessary electrostatic compensation may be attained by the entry of such cations as Ca^{2+} and Ba^{2+}, which are always present in alkali feldspars. The diadochic substitution, Ba^{2+}, $Al^{3+} \rightarrow K^{+}$, Si^{4+}, and the formation of the celsian molecule $[Ba(Al_2Si_2O_8)]$, is well known in the K-Na feldspars.

Moreover, it must be remembered that, even in the agpaitic rocks, the essential albite and the perthitic albite always contain a certain amount of the anorthite component ($CaAl_2$) because of the extensive diadochic substitution in the plagioclases according to the scheme: $Ca^{2+}Al^{3+} \rightarrow Na^{+}Si^{4+}$. This substitution will naturally disturb the (K, Na): Al = 1:1 relationship in the alkali feldspars towards a certain excess of Al, and will decrease the theoretical value of the agpaitic coefficient.

Obviously an experimental study is needed to determine the quantitative effect of such substitutions on the decrease in the theoretical value of the agpaitic coefficient.

We now present an analysis of the data using 0.85 as the theoretical value of the coefficient (Na) which was obtained empirically from a generalization of these data.

Group 'A' - agpaitic association -- (Na) > 0.85

(See appendix)

This association is characterized by an excess of Na over Al, after the formation of feldspars and feldspathoids. The deficiency of Al is compensated in this case by ferric iron which in the combination (Na^{+}, Fe^{3+}) goes to the formation of aegirine ($NaFeSi_2O_6$), riebeckite ($Na_2Fe_3Fe_2[Si_4O_{11}]_2 \cdot [OH]_2$,) and arfvedsonite ($Na_3(Fe, Mg)_4(Fe, Al)[Si_4O_{11}]_2 \cdot [OH]_2$). Moreover, the extra Na may enter into the rarer complex titano- and zirconosilicates, such as eudialyte, astrophyllite, rincolite, etc. However, these minerals are not essential and form most frequently when there is a great excess of Na over ΔAl.

In the common agpaitic rocks with a moderate value of (Na) of the order of 0.85 - 1.1, zircon, sphene, ilmenite and other simpler minerals form. But even in these rocks the content of magnetite is noticeably low, owing to the fixation of Fe^{3+} in aegirine and alkalic amphiboles. Together with the appearance of aegirine the disappearance of magnetite may evidently be considered as one of the most characteristic features of the agpaitic association. Part of Fe^{3+} and a considerable part of Fe^{2+} may enter into the iron-rich biotite-lepidomelane, which sometimes accompanies aegirine.

The deficiency of Al in relation to Na forces Fe^{3+} to enter into the dark minerals and naturally makes the formation of aegirine and basic plagioclase impossible. This is easily understood, for otherwise aluminous augite, magnetite and calcic plagioclase would form, and this is possible only for a different (K, Na): Al ratio.

Group 'B' -- Plumasitic Association -- (Na) < 0.85
(See Appendix)

This association is characterized by a deficiency of Na in relation to ΔAl after the formation of feldspars and feldspathoids. The excess Al in these rocks joins other cations, such as Ca^{2+}, Mg^{2+}, and Fe^{2+}. Sodium may be present, but only as an admixture or in the ratio Na: Al <1. The result is the formation of aluminous dark minerals, such as biotite, augite, and common hornblende. The combination $CaAl_2$ becomes possible in the anorthite component of the plagioclase, and this leads to the appearance of alumina-free (or alumina-poor) pyroxenes of the diopside-hedenbergite-augite series.

In these rocks, ferric oxide need not appear as a substitute for Al and is often bound in magnetite, which may be quite abundant.

In the rocks with (Na) near 0.85, the pyroxenes with a considerable content of the jadeite component may form with Na: Al = 1:1, or the slightly alkalic amphiboles transitional between the common amphiboles and the hastingsite-taramite group. Thus, the new form of the agpaitic coefficient, $\frac{Na}{Al - K} = (Na)$, gives a clearer expression of the paragenesis of the dark minerals in alkalic rocks. Moreover, it is more sensitive to the changes in the paragenesis than the older coefficient, $\frac{Na + K}{Al}$. This can be seen by comparing the two ratios as given in the appendix and in Fig. 1. In general, the values obtained from the two coefficients are proportional to each other and are often identical. However, the value (Na) = 0.85 strictly delimits the regions of plumasitic and agpaitic associations, while the ratio $\frac{Na + K}{Al}$ is in many cases the same for both. This follows from the tendency of the values $\frac{Na + K}{Al}$ to overlap each other. For the plumasitic associations this ratio tends to be too high (area I) as compared with the values of $\frac{Na}{Al - K}$ for the same compositions, and for the agpaitic associations (area II), too low.

It should be emphasized that it is generally understood that the formation of agpaitic and plumasitic associations in alkalic rocks does not depend on the absolute amounts of K, Na and Al, but is determined mainly by the ratio of these elements. Nevertheless, many investigators have remarked on the determining role of high Na content in the formation of aegirines and Na-amphiboles [1, 7, 10]. The dependence of the various parageneses represented by the values of $\frac{Na}{Al - K}$ on the weight percentage of Na_2O in the rocks is shown in Fig. 2. Clearly, a high Na_2O content does, in general, favor the formation of dark sodium-bearing minerals. But no less important is the fact that a whole series of rocks with high Na_2O content (from 13 to 7-8%) is characterized by the plumasitic association, and conversely many rocks with a relatively low Na_2O content (from 7 to 4%), contain aegirine and Na-amphibole. This relationship is true also of K_2O. Aegirine and alkali amphiboles are found in many essentially orthoclase syenites as well as in feldspathic urtites. On the other hand, V. A. Kononova [6] described a titanian ferroaugite from a soda-rich urtite of the Chik intrusion. Characteristically this urtite has (Na) = 0.83, a plumasite coefficient. Thus, the ratio of the alkalies does not by itself determine the association of dark minerals but only when it is related to Al. The important role of ferric iron in the formation of aegirine and alkali amphiboles has already been mentioned. Their formation, however, cannot be related to the content of Fe^{3+} or to the Fe^{3+}/Fe^{2+} ratio in the rocks.

The graph of Fig. 3 shows the dependence of different parageneses on the Fe^{3+}/Fe^{2+} ratio. Evidently in most cases compositions having the same Fe^{3+}/Fe^{2+} ratio have either agpaitic or plumasitic associations. It is clear that Fe^{3+} plays an active role in the formation of sodic dark minerals only when there is a deficiency of Al, i. e., when (Na) > 0.85. In this case, aegirine and alkali amphiboles appear even when the Fe^{3+} content is very low, as for example in the alkalic aplites (see Appendix). No special discussion will be given of the significance of such rock components as Ca, Mg and Si in the analysis of parageneses other than noting that the effect of the SiO_2 content is unimportant. Aegirine and the alkali amphiboles occur in granites as well as in strongly undersaturated rocks. The agpaitic coefficient in granites is usually less than 0.85, and therefore the agpaitic dark minerals are rather seldom found in granites. Evidently the normal granitoids may be considered as oversaturated with alumina with respect to soda and as having the usual plumasitic association, biotite-common hornblende. Only in some "alkalic granites," unsaturated with Al with respect to Na, may aegirine and alkalic amphiboles appear when (Na) > 0.85. To separate such granites from the group of "alkalic granites" (to which many petrographers refer biotite alaskites), they may be called *agpaitic* alkalic granites to distinguish them from the *plumasitic* alkalic granites carrying biotite or common amphiboles.

The Ca and Mg content will determine only the occurrence of this or that mineral species in both agpaitic and plumasitic associations. In any case, the alkalic rocks discussed in the present paper show a great range of Ca and Mg content, and independently of it were referred either to the agpaitic or plumasitic dark mineral association on the basis of the value of (Na) = $\frac{Na}{Al - K} \gtrless 0.85$. It may be expected that the agpaitic rocks with high Mg content will contain arfvedsonite rather than aegirine or riebeckite.

Finally, the importance of the coefficient (Na) in revealing the order of crystallization of minerals in the igneous rocks may be pointed out. As defined, the coefficient (Na) indicates the excess or deficiency of Na with respect to Al *after* the fixation of Al and the alkalies in the feldspars and feldspathoids in the ratio 1:1. This definition of the coefficient is justified by the observed associations. This means that we may speak of the feldspars and feldspathoids as being earlier than the dark minerals. In many cases, especially in the leucocratic syenites, this order can actually be proved. However, in other alkalic rocks, of the melanocratic type (monzonites, essexites, ijolites and others), the order of crystallization is different. For example, in monzonites, as a rule, plagioclase and pyroxene are definitely earlier than the K-Na feldspar and nepheline which fill the spaces among the idiomorphic crystals of pyroxene and plagioclase. But in these cases of the early separation of the dark minerals, the observed

Appendix

The Amounts of Na, K, Al, Fe^{2+} and Fe^{3+} are Recalculated to the Relative Number of Atoms

No.	Rock	Locality (author)	In wt. %					$\frac{Na+K}{Al}$	$\frac{Na}{Al-K}$	Fe^{3+}/Fe^{2+}	Dark minerals
			Al_2O_3	K_2O	Na_2O	Fe_2O_3	FeO				
			Group 'A'								
1	Ijolites and lujavrites (average) of 6 analyses)	Khibina [5]	16,87	3,50	8,23	4,78	4,42	1,00	1,03	0,98	Aegirine, aegirine-augite
2	Urtites (av. of 8 analyses)	"	26,94	6,19	13,48	3,05	1,26	1,07	1,09	2,23	Aegirine, aegirine-augite
3	Poikilitic aegirine syenites (av. of 7 analyses)	"	22,10	5,46	10,23	2,12	2,16	1,02	1,03	0,87	Aegirine
4	Foyaite (av. of 6 analyses)	"	20,62	4,48	9,68	2,29	1,35	1,01	1,01	1,56	Arfvedsonite aegirine
5	Khibinite (av. of 5 analyses)	"	22,14	6,01	9,85	2,89	1,29	1,02	1,03	2,00	Aegirine, arfvedsonite
6	Urtite	Lovozero [2]	27,50	3,02	14,49	3,04	0,57	0,98	0,98	5,42	Aegirine
7	"	"	28,13	3,34	15,10	2,70	0,28	1,01	1,01	8,50	"
8	Eudialyte lujavrite	"	15,95	5,28	9,66	6,79	1,30	1,35	1,55	2,45	Aegirine, eudialyte, alkalic amphibole
9	"	"	16,79	4,14	9,07	6,57	2,53	1,15	1,29	2,34	"
10	"	"	17,75	4,37	9,26	6,97	2,01	0,92	1,17	3,14	"
11	Porphyritic albite lujavrite (canadite)	"	19,11	8,31	7,46	1,34	0,96	1,08	1,21	1,23	Eudialyte, alkalic amphibole, aegirine
12	Leucocratic foyaite	Lovozero [2]	26,62	5,36	13,16	1,95	0,29	1,03	1,04	6,00	Aegirine and alkalic amphibole
13	Juvite	"	22,87	4,77	12,55	4,52	0,51	1,12	1,16	8,00	Aegirine, eudialyte
14	Tawite	"	21,74	1,34	16,28	6,80	1,20	1,30	1,32	5,06	Aegirine
15	Poikilitic nepheline sodalite syenite	"	22,73	3,80	12,36	2,19	1,73	1,07	1,09	1,16	Aegirine, alkalic amphibole
16	"	"	22,29	4,42	12,36	2,88	1,73	1,12	1,16	1,50	"
17	Lujavrite	Daly av. [3] 1933	16,33	3,78	10,45	6,95	3,01	1,30	1,40	2,09	Aegirine, eudialyte
18	Tinguaite	Sierra do Tingua [3]	19,07	6,84	9,41	5,57	—	1,2	1,32	—	Aegirine, alkalic amphibole
19	Umptekite	Daly av. [3]	16,65	5,45	6,53	2,41	3,85	0,99	0,99	0,56	Arfvedsonite, aegirine
20	Nordmarkite	"	16,81	5,62	5,76	1,08	2,71	0,92	0,87	0,37	Alkalic amphibole
21	Pulaskite	"	18,37	5,70	6,45	2,28	1,71	0,91	0,87	1,16	Diopside-aegirine, arfvedsonite
22	Solvsbergite	"	17,58	4,95	7,30	3,05	1,80	0,98	0,98	1,52	Aegirine, alkalic amphibole
23	Soda minette	Brogger [3]	14,95	4,45	5,43	4,09	5,70	0,92	0,89	0,65	Biotite, aegirine, aegirine-augite
24	Aegirine-augite granite	Svyatoi Nos [5]	14,43	6,04	4,90	1,10	0,66	1,02	1,03	1,40	Aegirine-augite
25	Nepheline syenite (Khibinitopod)	SW Tuva [11]	21,1	4,56	9,97	3,6	1,75	1,01	1,01	1,91	Aegirine, arfvedsonite

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Note: Comma represents decimal point.

Table (Continued)

No.	Rock	Locality (author)	In wt. %					$\frac{Na+K}{Al}$	$\frac{Na}{Al-K}$	Fe^{3+}/Fe^{2+}	Dark minerals
			Al_2O_3	K_2O	Na_2O	Fe_2O_3	FeO				
26	Alkalic syenite	SW Tuva [11]	16,41	7,84	5,67	0,53	1,43	1,14	1,18	0,31	Aegirine, arfvedsonite, riebeckite
27	Coarse-grained nepheline syenite	Bulankul' [5]	21,59	6,77	8,77	0,54	2,45	1,01	1,10	0,20	Riebeckite with pyroxene and biotite
28	Saibarite	Mt. Saibar [5]	16,35	4,41	9,31	—	—	1,20	1,30	—	Aegirine, kataphorite
29	Alkalic syenite	Mariupol' region [5]	15,92	0,42	10,98	4,94	0,11	1,16	1,16	61,00	Aegirine
30	"	"	15,42	1,08	11,27	4,75	0,28	1,4	1,31	14,70	"
31	"	"	16,35	6,36	6,04	2,02	1,28	1,03	1,05	1,33	Taramite
32	"	"	16,25	6,00	6,32	2,86	1,48	1,04	1,06	1,70	Augite-aegirine
33	"	"	15,03	3,88	6,98	3,67	1,66	1,06	1,06	1,90	"
34	Leucocratic mariupolite	"	18,72	0,79	11,77	3,26	0,34	1,09	1,09	8,40	Aegirine-augite
35	Gneissoid mariupolite with zircon	"	18,90	2,04	12,85	6,02	0,22	1,23	1,26	2,50	Aegirine
36	Fine-grained mariupolite with sodalite	"	21,49	2,21	13,25	2,07	0,93	1,12	1,13	2,16	"
37	Trachytoid foyaite	"	20,32	5,82	8,78	3,53	3,15	1,02	1,04	1,04	Taramite
38	Dense foyaite	"	18,57	5,77	7,97	2,08	4,29	1,05	1,07	0,43	"
39	"	"	18,27	4,87	9,71	6,13	0,81	1,16	1,23	6,90	Hastingsite, aegirine
40	Leucocratic foyaite	"	21,44	5,30	8,92	1,43	3,82	0,97	0,93	0,34	"
41	Melanocratic foyaite	"	21,46	5,20	8,71	1,88	5,22	0,92	0,90	0,33	"
42	Lestiwarite	Urals, Kashtymskaya [5] dacha	17,17	5,32	6,92	0,76	0,68	0,98	0,97	0,90	Aegirine-augite, hastingsite
43	Quartz syenite	"	15,25	5,64	4,78	1,02	1,67	0,91	0,86	0,50	Aegirine-augite
44	Hornblende miaskite	Il'men' Mts [5]	22.36	6,11	8,17	0,79	1,42	0,89	0,85	0,53	Hastingsite
45	Mica and hornblende nepheline syenites	Khibiny [5]	21,30	6,02	7,74	1,86	4,00	0,90	0,89	0,41	Lepidomelane, arfvedsonite
					Group 'B'						
46	Miaskite	Il'men' Mts [5]	22,34	5,16	8,44	1,13	1,63	0,86	0,82	0,63	Biotite
47	Foliated miaskite	Il'men' Mts, Vishnevye Mts, [5]	23,25	6,19	6,33	0,69	2,95	0,73	0,63	0,19	"
48	"	Mt. Sobach'ya	23,59	5,72	7,77	0,85	2,61	0,80	0,75	0,30	"
49	Quartz augite syenite	Il'men' Mts [5]	17,67	2,86	6,93	1,35	1,22	0,81	0,78	1,00	Augite
50	Alkalic melanocratic syenite	Urals, Kyshtymskaya dacha [5]	19,11	2,74	6,81	6,75	2,80	0,74	0,70	2,18	Aegirine-augite, biotite
51	Alkalic syenite	Mariupol' region, [5]	15,72	5,45	4,97	2,00	7,61	0,90	0,83	0,22	Hastingsite

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Note: Comma represents decimal point.

(Table Continued)

No.	Rock	Locality (author)	In wt. % Al_2O_3	K_2O	Na_2O	Fe_2O_3	FeO	$\frac{Na+K}{Al}$	$\frac{Na}{Al-K}$	Fe^{3+}/Fe^{2+}	Dark minerals
52	Granite	Mariupol' region [5]	14,53	5,43	3,31	0,15	1,34	0,70	0,62	0,06	Biotite
53	"	"	11,65	6,07	3,11	4,04	0,90	1,00	0,50	4,10	Diallage
54	"	"	13,53	4,91	2,92	5,01	4,80	0,75	0,58	0,90	"
55	Fine-grained nepheline syenite	Bulankul' [5]	23,76	5,56	8,74	—	—	0,86	0,81	—	Pyroxene, biotite, riebeckite
56	Nepheline syenite (miaskite)	S. E. Tuva [11]	20,68	7,22	5,70	1,24	5,74	0,82	0,72	0,18	Hastingsite, biotite
57	Ijolite-urtite	Tuva, Dakhunur [6]	23,75	3,04	10,42	2,87	4,22	0,86	0,84	0,62	Ti-ferroaugite
58	Urtite	Tuva, Chik [6]	29,25	6,00	11,60	1,05	1,60	0,87	0,83	0,60	"
59	Ijolite-urtite	"	23,41	3,3	6,28	2,47	5,81	0,60	0,54	0,39	"
60	Ijolite	"	15,85	1,69	5,07	2,01	10,07	0,64	0,60	0,17	"
61	Essexite-porphyrite	Lovozero [2]	13,74	2,09	2,84	6,00	7,60	0,50	0,40	0,71	Ti-augite
62	Akerite	Daly av. [3]	17,07	3,80	4,65	2,35	3,37	0,68	0,59	0,61	Diopside
63	Monzonite	"	16,96	3,76	3,67	2,93	4,01	0,6	0,46	0,64	Augite, biotite hypersthene, olivine
64	Minette	"	14,41	4,69	2,54	3,39	5,01	0,64	0,45	0,60	Biotite
65	Vogesite	"	14,86	2,83	3,21	3,60	4,18	0,56	0,46	0,80	Common hornblende, augite
66	Monmouthite	Adams [3] ,,	30,59	3,88	13,25	0,44	2,19	0,87	0,84	0,19	Hastingsite
67	Beresite	Erdmannsdorffer [3]	23,66	2,6	8,94	4,79	3,28	0,74	0,71	1,30	Ti-augite with aegirine-augite rim
68	Larvikite	Daly av. [3]	21,11	3,87	5,89	2,89	2,39	0,65	0,57	1,09	Ti-augite, diopside, barkevikite and lepidomelane
69	Viterbite	Italy [3]	20,75	10,47	2,86	1,71	2,19	0,77	0,50	0,74	Augite, diopsidic augite
70	Calc-alkalic hornblende syenite	Daly av. [3]	15,28	4,41	3,10	2,59	3,47	0,64	0,48	0,65	Common hornblende
71	Augite syenite, calc-alkalic	"	18,77	2,99	4,35	6,11	3,26	0,55	0,46	1,70	Augite, biotite
72	Monzonite-essexite	Sandyk massif (author)	15,44	5,45	2,55	3,10	4,49	0,65	0,43	0,60	Augite, biotite olivine
73	Calcic syenite	"	17,26	6,12	3,05	2,33	3,66	0,67	0,47	0,56	Augite-salite, biotite
74	Hornblende alkalic syenite	"	19,75	10,02	3,40	1,34	2,31	0,83	0,63	0,50	Common hornblende
75	Nepheline syenite	"	20,51	12,44	2,32	1,27	1,43	0,84	0,54	0,83	Biotite with admixture of diopsidic augite
76	Psuedoleucite nepheline syenite	"	19,67	12,84	2,39	0,98	2,45	0,91	0,69	0,35	Common hornblende, biotite, augite-salite
77	Syenitic aplite	"	16,11	8,44	3,72	1,13	0,47	0,94	0,87	2,00	Aegirine-augite

Note: Comma represents decimal point.

parageneses also justify the use of the coefficient (Na). In light of these facts, the interesting statement concerning the crystallization of magmas made by Loewinson-Lessing becomes very probable: "While the magma was still liquid, the bases divided the silica among themselves and formed compounds according to the degree of their affinity for each other, according to their need, as it were. As for the order of separation of minerals from the magma, it is independent of this distribution of the bases but is determined by the law of mass action and the requirements of equilibrium for a given composition of the system, temperature and pressure" [7]. It may be concluded from this that the value of the coefficient (Na) $\lessgtr 0.85$ cannot determine the order of crystallization of the dark minerals from the melt. It can indicate only whether the dark mineral association is agpaitic or plumasitic. The idea that only the agpaitic rocks are characterized by the agpaitic order of crystallization with late separation of dark minerals is evidently erroneous.

It may be assumed that in both agpaitic and plumasitic alkalic rocks the dark minerals may crystallize either early or late, depending on the proportion of the femic components (Mg^{2+}, Fe^{2+} and Fe^{3+}) and Ca, on the one hand, and the salic (K and Na) components on the other. The investigation of this problem is a separate large undertaking. The results of application of the proposed (Na) coefficient bear out Loewinson-Lessing's opinion concerning the probable distribution of the components of a magma during the pre-crystallization period of cooling relative to the composition of future minerals. The coefficient (Na) must be used with reliable analyses of alkalic rocks. On the other hand, if the mineralogy of a rock is known, the agpaitic or plumasitic value of (Na) derived from the chemical analysis may serve as a check on the analysis.

Summary

1. The ratio $(Na) = \frac{Na}{Al - K} = \frac{Na}{\Delta Al}$ shows whether there is an excess or deficiency of Na with respect to the remainder of Al after its fixation by potassium. This is the main condition for the appearance of agpaitic or plumasitic dark mineral associations in alkalic rocks. The ratio may be used instead of the generally accepted agpaitic coefficient, $\frac{Na + K}{Al}$, which does not differentiate unequivocally between the two associations.

2. The standard value of the agpaitic coefficient, usually taken as one, is actually 0.85 for the $\frac{Na}{Al - K}$ ratio and approximately 0.9 for the $\frac{Na + K}{Al}$ ratio. The lower value of the coefficient may be due to an excess of Al in the alkali feldspars and nepheline over the alkalies, which permits diadochic substitution of Ba^{2+} and Ca^{2+} in these minerals.

3. The agpaitic alkalic rocks are those in which $(Na) > 0.85$, and the plumasitic (or miaskitic in the case of nepheline syenites) are those in which $(Na) < 0.85$. The most typical dark minerals in the agpaitic rocks re aegirine and soda amphiboles, and in the plumasitic, biotite, augite, common amphiboles and magnetite.

4. The new form of the agpaitic coefficient, $\frac{Na}{Al - K}$, is more sensitive the changes in the parageneses of minerals than the $\frac{Na + K}{Al}$ ratio.

The value of the latter is lower for the agpaites and higher for the plumasites as compared with the values of $\frac{Na}{Al - K}$ for the same rocks. The values of the old coefficient for different associations tend to overlap whereas the values of the proposed coefficient do not.

5. The presence or absence of aegirine and soda amphiboles in the alkalic rocks is not determined by the absolute content of Na_2O, Fe_2O_3 or the Fe^{3+}/Fe^{2+} ratio, but depends on the ratio of Na and K to Al.

6. It is proposed that the alkalic granites be subdivided into agpaitic, with $(Na) > 0.85$ and containing aegirine or alkali amphiboles, and plumasitic, with $(Na) < 0.85$, containing biotite and common amphiboles. A similar division of alkalic syenites would also be useful.

7. The new form of the agpaitic coefficient, $(Na) = \frac{Na}{Al - K}$, is in agreement with Loewinson-Lessing's hypothesis of distribution of the elements in the melt into groups corresponding to the composition of the future minerals during the period preceding the crystallization of the magma. It is doubtful that crystallization with the formation of the dark minerals at the end of the process is characteristic of the agpaitic rocks only.

There is no doubt that a number of questions discussed in this paper are controversial, and the author hopes that critical comments and new data will help to answer them.

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BIOGEOCHEMICAL INVESTIGATIONS IN KADZHARAN, ARMENIAN SSR

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The use of the biogeochemical method in different parts of the USSR proved its effectiveness in the search for nickel and copper-molybdenum deposits [1, 2]. The investigations in Kadzharan showed that the copper-molybdenum sulfide ores are continuously attacked by meteoric waters, often causing the oxidized zone to extend to a considerable depth. The upper part of the Kadzharan deposit (town of Pirdoudan on the left bank of the Okhcha River) is composed of unconsolidated products of weathering (eluvium and hill wash) which often preserve the structure of the parent rocks responsible for the mineralization--monzonites and adesites.

The dispersion aureoles of the copper-molybdenum ores on the left bank of the Okhcha River were outlined by the authors as early as 1955 on the basis of the high copper and molybdenum content in soils and plants. Drilling in the area in 1957-1958 showed that the ore zones lying at a depth of 0-50 m correlate well with the anomalies discovered on the surface. This indicates a constant and rather intimate geochemical connection between the ore and the surface materials. The dispersion aureoles appear on the surface due to the hydrogeological conditions of the region and the activity of plants. A concrete illustration of the latter is the accumulation of metals in the humic horizon of the soil. The use of plants and of the upper soil layer in prospecting is a specific characteristic of the biogeochemical method which distinguishes it from the metallometric survey and from other geochemical methods.

Geobotanical observations may be of considerable help in determining the presence of ore in a new territory. In the present paper we wish to share our experience in this type of prospecting by describing our investigation at the Kadzharan copper-molybdenum deposit and at the Atkyz (village Okhcha) polymetallic deposit.

In carrying out a biogeochemical survey for copper and molybdenum on the left bank of the Okhcha River in Kadzharan, now the Karmir-Kara mineralized area, we noticed the localization of certain types of steppe vegetation to certain rocks and ore zones.

At the Karmir-Kara area, in spite of the very complex association of effusive and intrusive rocks, andesites, monzonites and syenites, the outer contours of the rocks are very easily traced by means of soils and plants. Dark-brown soils are developed on the weathered monzonites, while on the andesites and hornfelses the soils usually have a greenish-gray tinge. The plant associations growing on these soils differ from each other in outward appearance and in species composition.

The geobotanical mapping of the Karmir-Kara area showed a rather intimate connection between individual plant associations and the outcrops of certain rocks. A comparison of the geological and geobotanical maps of the area (1:2000) (Figs. 1 and 2) shows that the thyme-tragacanth association is restricted to the monzonites; the varied assemblage of leguminous plants, to the andesites; and so forth.

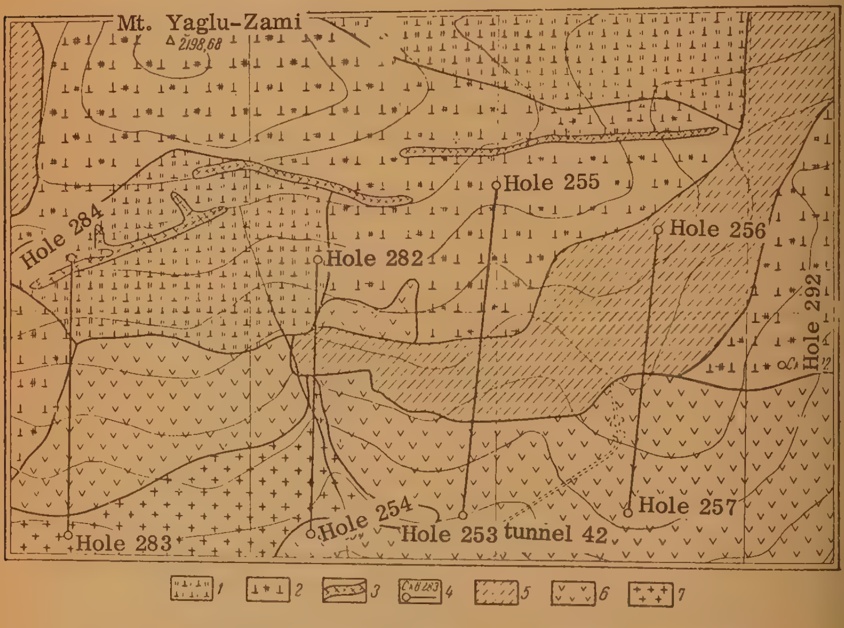

Fig. 1. Geological sketch map of the Karmir-Kara area

1 -- slightly altered andesites, 2 -- strongly altered andesites, 3 -- granodiorite porphyry dikes, 4 -- geological sections based on drillholes, 5 -- hornfelses, 6 -- unaltered monzonites, 7 -- syenites

It was noticed also that the drooping astragalus (Astragalus declinatus W.) grows mainly over the zones of hydrothermal mineralization. This is especially clearly seen on Mount Pirdoudan, in the main copper-molybdenu deposit, and on the left bank of the Okhcha River (Karmir) Kara and Davac areas) where the soils are enriched in copper and molybdenum [3]. Here, drooping astragalus is a constant component of the grass cover. A chemica analysis of the astragalus plants collected over the ore zone shows a high content of copper and molybdenum, several times higher than in plants

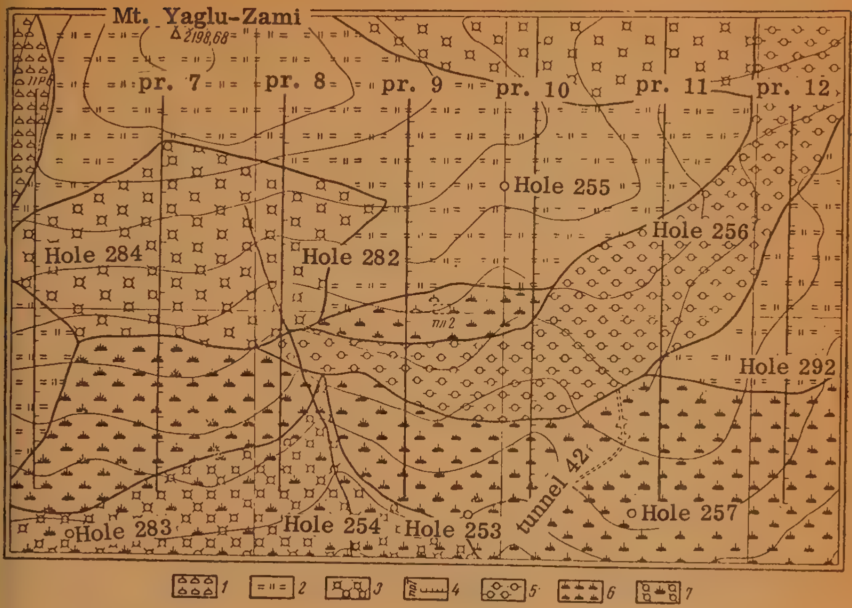

Fig. 2. Geobotanical sketch map of the Karmir-Kara area

1 -- Silene compacta F. association, 2 -- cereals and various grasses, 3 -- leguminous plants and various grasses, 4 -- biogeochemical profile, 5 -- Lapsana communis L. association, 6 -- thyme-tragacanth association, 7 -- thyme-tragacanth association with leguminous plants

growing outside of the mineralized area (geochemical background). As can e seen from the data of Table 1, the roots of the drooping astragalus have particularly high molybdenum content.

The accumulation of molybdenum in the roots of the astragalus agrees ith Kh. G. Vinogradova's data [4] on the concentration of this element by he nitrifying bacteria on the roots of leguminous plants. Molybdenum is oncentrated also by other plants growing over molybdenum deposits--by igwort, common nipple wort and St. Johnswort. Therefore, the localization of the drooping astragalus to the copper-molybdenum ores of Kadzharan annot be explained by the high molybdenum content in the soil alone. The ffect of the entire soil, climate and geochemical complex characteristic of he region must be taken into account.

THE VARIATION IN THE POPPY--PAPAVER COMMUTATUM F. et M.

Further biogeochemical observations at the Karmir-Kara area showed riation in the development of black spots on the petals of the poppy, paver commutatum. In the normal forms the purple-red petals of the

Table 1

Copper and Molybdenum Content in the Ash of Plants Growing over Ore Deposits

No. of sample	Time and locality of sampling	Content in ash, %		Cu/Mo
		Cu	Mo	
264	Drooping Astragalus, Karmir-Kara mineralized area, profile 8-9 (July 1958), leaves	0.034	0.011	3.0
	Same, root	0.027	0.152	0.2
151	Golden astragalus, Karmir-Kara mineralized area, profile 8-9 (July 1958), Stem and leaves	0.031	0.024	1.3
	Root	0.041	0.088	0.5
386	St. Johnswort, Karmir-Kara mineralized area, (August 1958) Exposed parts	0.070	0.027	2.6
647	Common nipple wart, Karmir-Kara mineralized area, profile 9 (July 1955) Stems and leaves	0.125	0.015	8.3
385	Transcaucasian thyme Stems and leaves	0.114	0.015	7.6
300	St. Johnswort, on the road to Kaputzhikh (far from the mineralized zone) (August 1959) Exposed	0.011	0.004	2.8
301	Golden astragalus, on the road to Kaputzhikh (far from the mineralized zone) (August 1959) Exposed parts	0.011	0.007	1.6

flower have one black spot at the base. In the modified forms the spots are strongly elongated, reach the end of the petal and form a black cross. Fig. 3 shows the normal and modified forms of the poppy flower.

The modified poppy was found in the gully between profiles 8 and 9 of the exploration grid (Fig. 2) where the soils are fed by ground water enriched in copper and molybdenum [3]. The high content of these metals in the soil soil moisture and plants is evidently one of the causes of change in the coloration of the poppy petals.

The change in the color of flowers effected by chemical factors is a fairly common phenomenon. It is well known from horticultural practice that addition of manganese salts to the soil enhances the color of carnations, asters and some other flowers. The flowers of hydrangea change from pink to blue on addition of ammonia alum to the soil. According to Jensch [5] an excess of zinc in the soil changes the blue color of the corolla

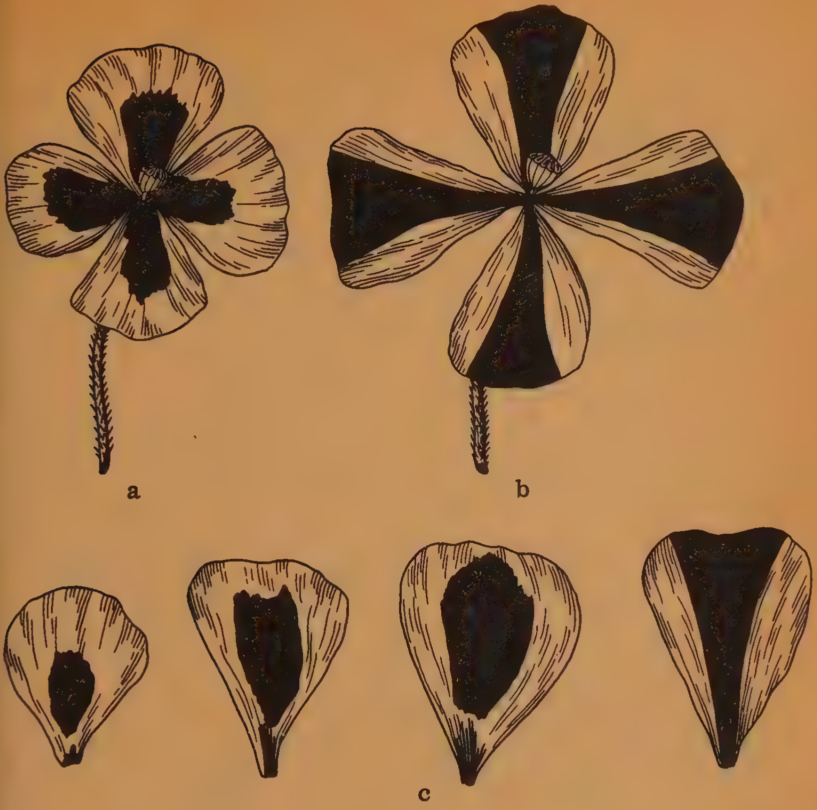

Fig. 3. Variation in the pigmentation of the flowers of *Papaver commutatum* F. et M.

a -- normal flower, *b* -- modified flower, *c* -- stages in the modification of the petals

to a yellow and red. In the experiments of N. A. Bazilevskaya and Z. A. Cibertseva [6], with Mn, Zn, B, Cu and other salts, the orange color of the *Eschscholzia* changed to red, etc.

A relatively low copper and molybdenum content--0.021% and 0.006%, respectively--in the ash of the modified *P. commutatum* makes it impossible to ascribe the observed change entirely to the presence of these elements. Besides the presence of the ore minerals there are local geochemical factors, such as the relative wetness of the soil in the area of ground water seepage, lower pH of the waters and others which may plan an important role in modifying the pigmentation of the flowers.

Our experience in using the color change in flowers in the search for ore is very limited. Therefore gathering of data in this field has an important scientific and practical importance.

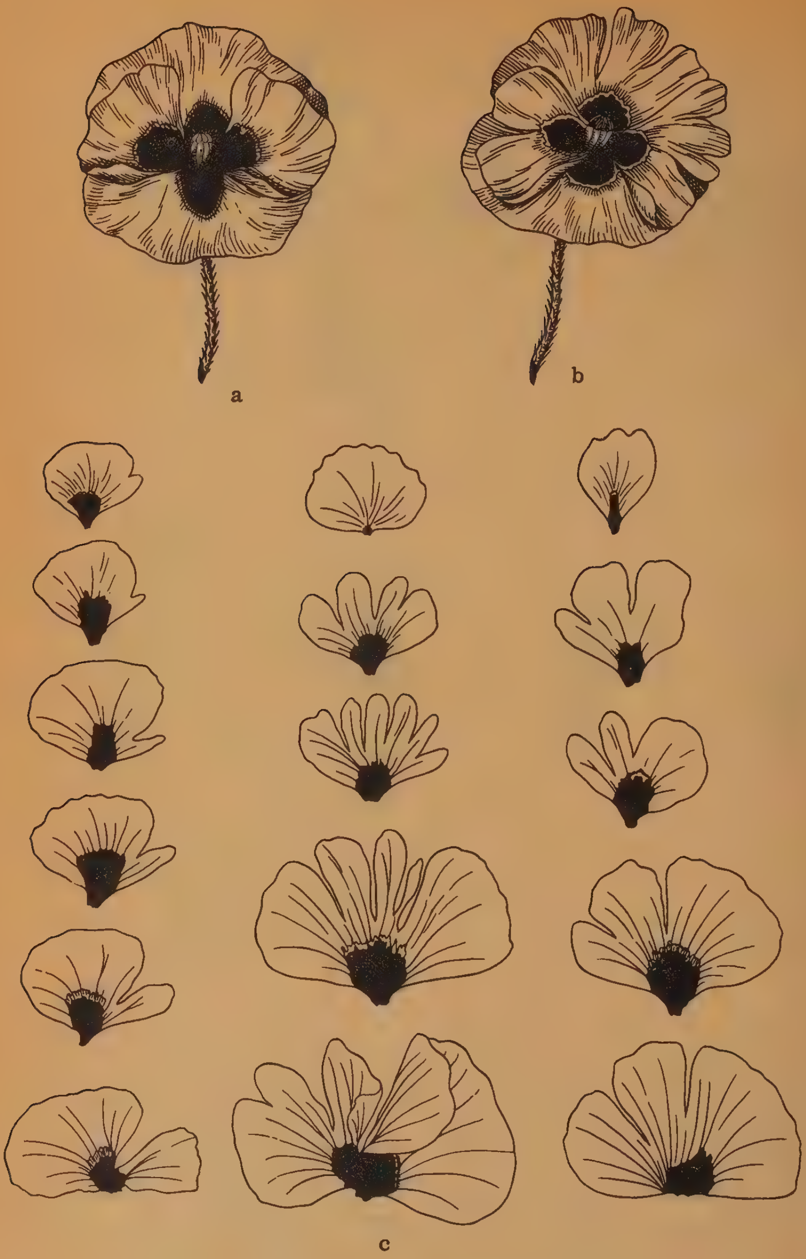

Fig. 4. Variation in the petals of the large-pod poppy (*Papaver macrostomum* B et H)
a -- normal flower, *b* -- modified flower, *c* -- stages in the modification of the petals

VARIATION IN THE LARGE-POD POPPY (*PAPAVER MACROSTOMUM* B. et H.) AT THE AKTYZ POLYMETALLIC DEPOSIT

At the Aktyz copper-lead-zinc deposit, modified forms of the large-pod ppy were found, showing variation in the lobation of the petals of the rolla. In the USSR this type of poppy is found mainly in the Caucasus, in menia and Azarbaijan. It is characterized by broad, almost kidney- aped petals with smooth edges.

In the modified poppy the petal edges are lobate and the flowers vary eatly in the degree of lobation and the number of lobes (See Fig. 4). All adations may be seen, from slightly lobate to strongly lobate petals pro- cing the illusion of extra petals. In some specimens the petals are divided

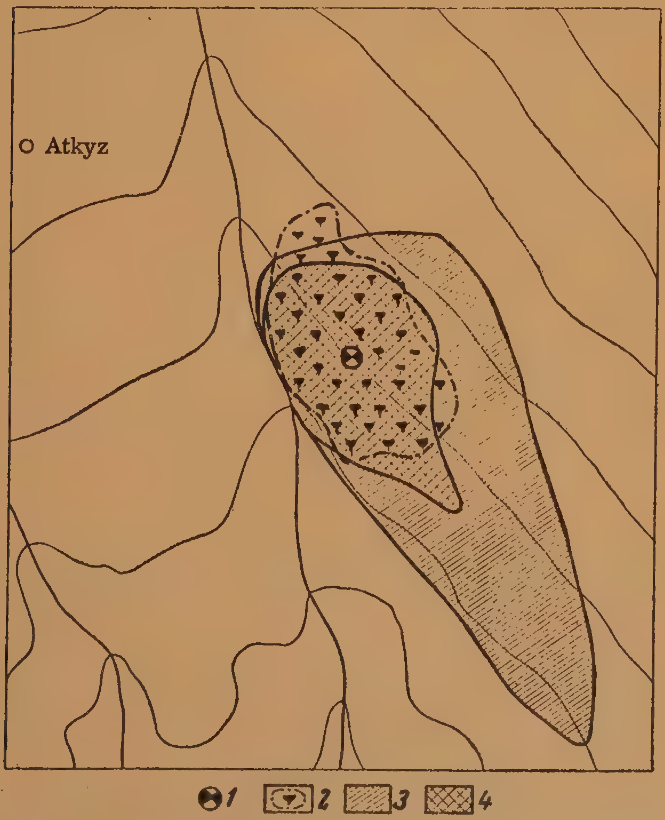

Fig. 5. Distribution of modified poppy at the Atkyz polymetallic deposit

1 -- deposit, 2 -- modified form of large-pod poppy, 3 -- lead content in soil 0.001%, 4 -- lead content in soil 0.01%

to the base, and forms with "double" flowers having from 5 to 7 instead of the normal 4 petals appear.

The modified forms of the large-pod poppy are found in the areas of the Atkyz deposit with high copper, lead and zinc content in the soil. The copper content in the soil of this area is $4.2 \cdot 10^{-2}$, of lead -- $2.3 \cdot 10^{-2}$ and of zinc -- $1.6 \cdot 10^{-2}$%.

The localization of the modified forms of poppy in the dispersion aureole of the ore minerals is shown in Fig. 5.

In searching for the cause of variation in the large-pod poppy growing over polymetallic deposits, we analyzed the flowers for copper, lead and zinc. The analyses are given in Table 2.

Table 2

Cu, Zn and Pb Content in the Ash of Large-Pod Poppy

No. of sample	Plant, place and time of sampling	Content in ash, %		
		Cu	Zn	Pb
1	Large-pod poppy, normal, Atkyz, ore zone (July 1958) Stems, leaves and flowers	0.016	0.006	0.003
2	Large-pod poppy, modified, Atkyz, ore zone (July 1957) Stems, leaves and flowers	0.012	0.031	0.015
3	Large-pod poppy, normal, Karmir-Kara area, near borehole 255 (July 1958) Stems, leaves and flowers	0.294	0.003	0.004

The analyses show a high content of the elements present in the deposit--Cu, Pb and Zn. It is important to note that the ash of the modified poppy has five times the normal content of zinc and lead and nearly normal copper content.

In the Karmir-Kara area of the copper-molybdenum deposit where zinc and lead are not abundant, occasional specimens of the modified poppy were found (2 out of 50). The phenomenon just described must be considered as an interesting case of the effect of lead and zinc on plants growing in mineralized areas.

There is an extensive literature on the effect of zinc on plants. W. M. Carton [7] mentions that an addition of 0.05 mg of zinc per one liter of nutrient solution causes scaling of tomato skins. Something like this was observed by us in the modified large-pod poppy at the Atkyz polymetallic deposit. Fig. 6 shows transverse sections through the peduncle of the normal and modified flowers. In the modified form collected at the deposit, the walls of the phloem are obliterated. Some of the sieve tubes are atrophied and the remaining ones are considerably enlarged (4, Fig. 6). There

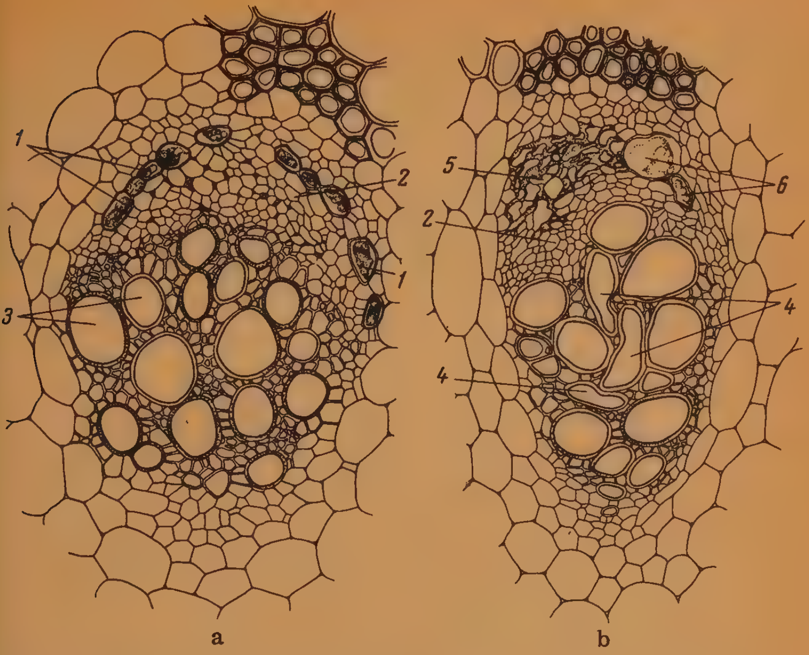

Fig. 6. Cross section of the fibrovascular bundle of the peduncle of *Papaver macrostomum* B. et H.

a -- normal flower, b -- modified flower: 1 -- sap canals, 2 -- phloem
3 -- conducting vessels, 4 -- deformed vessels, 5 -- obliteration of phloem cells and sap canals, 6 -- deformed sap canals

s also a change in the form of the vascular bundles.

The modification of plants caused by the high metal content in the soils eveloped over ore bodies is documented at present by numerous facts. his phenomenon permits a wide use of a simple and accessible indicator n the search for ores.

Summary

1. A biogeochemical localization of plant associations to the definite pes of intrusive and extrusive rocks has been established: the thyme-agacanth association is found over monzonites and the assemblage of eguminous plants, over andesites.

2. There is a preferential development of the drooping astragalus *Astragalus declinatus* W.) on the hydrothermal copper-molybdenum zones. The molybdenum content in the plant roots reaches tenths of one percent n ash).

3. A modified form of the poppy *Papaver commutatum* F. et M. with

unusual development of black coloration on the petals (black cross) was found. This form is localized on ground water seepages enriched in copper and molybdenum at the Karmir-Kara area of the Kadzhar deposit.

4. The variation in the large-pod poppy (Papaver macrostomum B. et H.) growing over the Atkyz polymetallic deposit in the Kradzhar region has been studied. The change in the petals of the poppy consists in the various degrees of lobation. The extreme forms have additional petals (double flower) not usually found in this species of poppy.

5. The ecological variations in plants growing over copper-molybdenum and polymetallic deposits may have theoretical and practical (prospecting) significance.

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CERTAIN CHARACTERISTICS OF THE GEOCHEMISTRY OF MOLYBDENUM IN THE SOILS OF CENTRAL KAZAKHSTAN

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The material presented in this paper was obtained by an analysis of the metallometric data for the area located in Central Kazakhstan 80 km east of the town of Karkaralinsk. Exploratory work which included metallometry on a 500 x 50 m grid disclosed in this area extensive dispersion aureoles containing 0.001 - 0.02% of molybdenum and sometimes more. Metallometric samples were collected in August and September of 1955.

Later, within the molybdenum dispersion aureoles covering an area of about 200 km^2 in the contact zone of the Bokhta granitic intrusion, a number of molybdenum-bearing quartz veins, veinlets and greisen were found.

During the reexamination of the molybdenum dispersion aureoles in June-July of 1956, along the same exploratory profiles, 1000 more metallometric samples were collected (10-20% of the total number of samples collected in 1955). About 25% of the samples from the second collection were taken from areas covered by overburden (areas of low relief) and about 10% from the rest of the aureole area.

In comparing the analyses of the samples collected in 1955 and 1956, it was found that in some areas the content of molybdenum in the 1956 samples differed by a factor of three or more from that in the 1955 samples taken at the same points. In other areas of the aureole the difference in the molybdenum content in the 1955 and 1956 samples was within the limit of error of the semiquantitative spectrographic analysis. To eliminate the possibility that the differences were due to analytical error, both sets of samples were analyzed spectrographically once again, and about 200 samples from both sets were subjected to chemical analysis. The results of the latter agreed, with deviations due merely to the difference in the precision of the method, with the results obtained by spectrography.

Fig. 1 represents the molybdenum dispersion aureoles plotted according to the data of 1955 only since it is impossible to construct an equally accurate and detailed map of equal concentrations of molybdenum on the basis of the incomplete sampling of 1956.

For this reason, the change in the content of molybdenum in the soils is illustrated not by a map but by a profile across a dissemination aureole. As an example, Fig. 2 shows a segment of profile 62 with the results of

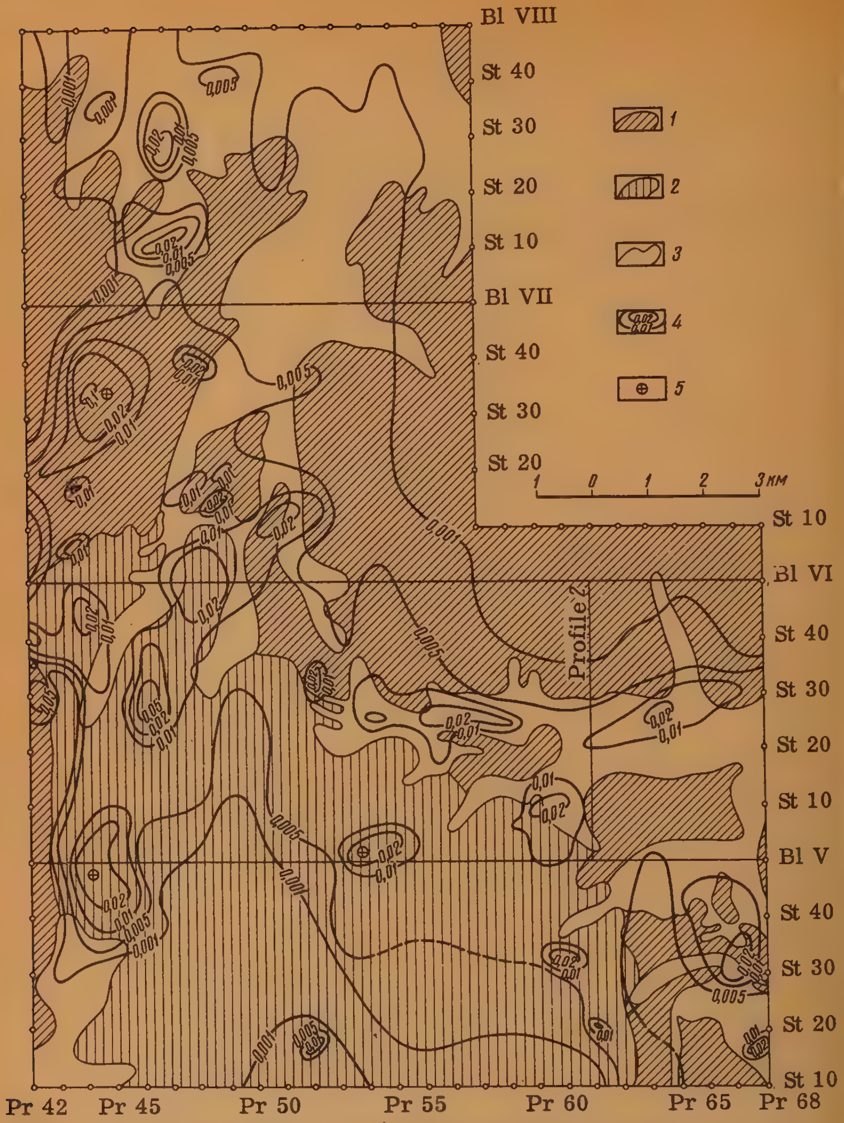

Fig. 1. Map of molybdenum dispersion aureoles (scale 1:100,000)

1 -- area of high relief with granite outcrops (autonomous landscapes); 2 -- low hills and foothill areas. Residual soil and hill wash usually 0.5 - 5 m thick; 3 -- transitional areas between foothills and valleys, valleys and other negative relief forms covered with unconsolidated sediments (subordinate landscapes); 4 -- equal concentrations of molybdenum according to metallometric survey on 1:50,000 scale (%); 5 -- main primary molybdenum mineralization; profile numbers (every fifth Pr) are marked on the horizontal border; stake numbers (every tenth), on the vertical border.

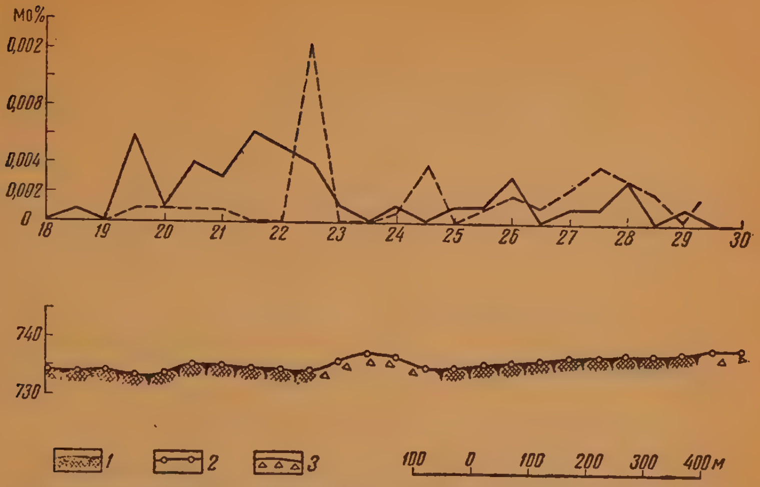

Fig. 2. Molybdenum content along profile 62 (base lines V-VI) in the samples collected in 1955 (solid line) and in the samples collected in 1956 (interrupted line) according to the data of chemical analyses. Stake numbers are marked on the horizontal.

1 -- surface relief; 2 -- points at which metallometric samples were collected; 3 -- soil layer with fragments of weathered parent rock.

chemical analyses of samples collected in 1955 and 1956. Here, between stakes 18 and 22, over a distance of 400 m, the average molybdenum content in the soils at the end of the summer of 1955, according to the chemical analyses, was 0.003%, but in the summer of 1956, it was less than 0.001%, of the order of 0.0004ii. According to the spectrographic analyses, the corresponding values were 0.004% in 1955 and of the order of 0.0003% in 1956. (In calculating the average content, all samples containing less than 0.001% Mo, i.e. less than the reliable limit of sensitivity of analysis, were considered as molybdenum-free). In another 250 m segment of profile 62, between stakes 19 - 50 and 22, the average molybdenum content in 1955, according to the chemical analyses, was 0.004%, while in 1956 it was of the order of 0.0007%; i.e., it decreased more than five times.

Side by side with the decrease in the molybdenum content in the soils in 1956, an increase in it occurred in some cases, for example in the samples taken at the stakes 22 + 50 and 24 + 50, located in the zones of accumulation of material washed off from a slightly elevated area.

In the remaining part of profile 62, located on a gentle slope, no changes in molybdenum content were observed. Similar results were obtained along a number of other profiles where additional samples were collected in 1956.

On the basis of these data, the area of molybdenum dissemination aureoles (Fig. 1) was divided according to its geomorphic and geological features into three regions in whose soils molybdenum exhibited different behavior in 1955 and 1956.

a) The region of granitic outcrops with a thin cover of hill wash and sparse grass cover (autonomous landscape of A. I. Perel'man [4]). Here there was no change in the molybdenum content during the period between the two samplings in 1955 and 1956 (more precisely, the average change is below the sensitivity of chemical analysis).

b) The valleys and other negative relief forms covered by 5-10 m of overburden. With rare exceptions, these areas are drained only in spring and the surface may be moist even in summer after a heavy rain. The deficiency of precipitation and the semiarid climate favor precipitation of salts in the soils to a greater or less degree and sometimes even the formation of salt marsh. These are Perel'man's subordinate landscapes [4]. It is precisely here that the results of the second sampling show the maximum difference in the molybdenum content in soils, usually a decrease in it in 1956 and very infrequently an increase.

c) The low hills and foothill slopes. The bedrock is covered by 0.5 to 5.0 m of weathered mantle and hill wash; the soils are normal. Here the molybdenum content in the soils changed by less than a factor of 2 during the same period, so that these changes are intermediate between the changes in the other two regions.

Such are the facts derived from the analyses and the field data. It should be added that the metallometric surveys in Central Kazakhstan often showed concentrations of molybdenum in the areas of low relief and especially in salt marshes several kilometers distant from molybdenum mineralization. Soils with molybdenum concentrations up to 0.01% were found in the valley trending east-west between the base lines $\underline{V}$ and $\underline{VI}$ and elsewhere (Fig. 1).

Thus in a semiarid climate there are two distinct types of concentration: (1) in the immediate vicinity of primary mineralization in the clastic materials resulting from weathering and spread about by a purely mechanical process; and (2) the distant concentration formed by the migration of the easily soluble molybdenum salts into the negative forms of relief. The formation of such concentrations presupposes repeated solution of the molybdenum salts. This may occur as a result of heavy rains, change in the water table, etc.

The difference in the regime and amount of precipitation in the spring and summer of 1955 and 1956 is the cause of the observed change in the molybdenum content in the soils. According to the records of the Karkaralinsk meteorological station, 80 km distant from the area, the precipitation in 1955 was 135.2 mm and in 1956, 233.5 mm. During the spring-summer period, April to July, immediately preceding sampling the amount of precipitation was 66.7 in 1955 and 174.6 in 1956, i. e. almost three times as much in 1956.

In general, molybdenum occurs in the unconsolidated sediments and soils in three different forms: in compounds practically insoluble in water, in compounds more or less easily soluble in water, and as salts dissolved in the soil moisture and ground water.

Depending on the climate and natural conditions, and especially on the amount of precipitation, relief and location with respect to the drainage system, one or another of the forms will predominate in the soils of each particular area. The soluble form predominates in the areas of low relief and saline soils. These concentrations of molybdenum change with the regime and amount of precipitation. When precipitation increases sharply, as in 1956, the content of molybdenum in the soils decreases.

The soils of Central Kazakhstan are characterized by the occurrence of a large part of molybdenum in the form of soluble salts. The intensive eaching of molybdenum from the oxidized zones of molybdenum deposits as been pointed out by F. V. Chukharov [6] and a number of other investiators. The hydrochemical and biogeochemical studies indicate that molyblenum is stable in solutions over a broad range of pH values, composition f other salts in the solutions, their concentration, etc. There are the onclusions of E. E. Belyakova [7], N. I. Dolukhanova [2, 7] and other nvestigators.

Summary

The main characteristics of the geochemistry of molybdenum in the soils f Central Kazakhstan are:

1. A considerable part of molybdenum present in soils occurs in the orm of soluble compounds. This molybdenum is derived from the oxidized ones and is continually replenished.

2. The following features are observed in the separation of the soluble rom the insoluble molybdenum compounds:

a) The areas of high relief with immature soils have small amounts of oluble molybdenum (less than 5% of the total).

b) In the valleys and other negative landscape forms the soluble molybenum salts are concentrated with other easily soluble salts. The amount f soluble molybdenum may reach 100% of its total content.

c) The gentle foothill slopes and small hills occupy an intermediate osition between these two extremes.

3. The concentration of mobile molybdenum in the negative landscape orms isolated from the mineralized areas may reach several hundredths f one percent. The fluctuation in the concentration of molybdenum in me, the several-fold change in its content depends on the amount and reime of precipitation.

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URANIUM AND THORIUM IN THE GRANITOIDS OF THE MIDDLE DNEPR REGION

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The study of the radioactive elements in the acid igneous rocks or ranitoids is one of the most important problems of geochemistry. The ranitoids are the most widespread of the intrusive igneous rocks. They ave the highest uranium and thorium content and are of prime importance n the study of the mineralogy and geochemistry of these elements. In the nvestigations of Precambrian terrains characterized by the wide developnent of granites and by the complexity of geological structure resulting rom repeated regional metamorphism, ultrametamorphism, granitization, nd intrusive activity, geochemical data on the radioactive elements are specially valuable.

We have investigated the granitoids of the middle Dnepr region, geohemically one of the most interesting areas of the Ukrainian crystalline hield.

The object of the investigation was to measure the uranium and thorium ontent in the principal types of granitoids, to determine the characteristic ssemblages of accessory minerals and to discover what particular minrals carry the radioactive elements in the three granitoid complexes of ifferent ages occurring in the region.

The rocks were sampled by selecting specimens with peak radioactivity nd then preparing mixed samples—a method widely used in geochemical ivestigations [1, 2]. Uranium and thorium were determined in the Laboraory of Geochemistry of Radioactive Elements, Radium Institute, by the ell known procedure of dissolving the samples and measuring radium and orium emanations on electrometers of the SG-IM type. The accuracy of etermination by this method is ± 10%. Brief descriptions of the granitoids d the results of geochemical study are presented below.

The Precambrian crystalline shield of the Ukraine in the middle Dnepr egion is composed of several types of granites which can be separated into ree groups or complexes according to their ages.

1. The oldest (pre-Krivoi Rog) is the group of granodiorites and plagioanites of different ages.
2. The next is the Kirovograd-Zhitomir complex of gray biotite granites.

3. The youngest is the Takovskii complex of red microcline granites. Besides differing in age, the granites of these three complexes differ in chemical composition (Table 1) and origin.

Table 1

Average Chemical Composition of the Granitoids of the Middle Dnepr Region

Oxides	I The oldest complex (average of 12 analyses), %	II Kirovograd-Zhitomir (average of 14 analyses), %	III Tokovskii complex (average of 22 analyses), %
SiO_2	67,87	68,91	73,07
TiO_2	0,37	0,33	0,20
Al_2O_3	14,93	15,22	14,09
Fe_2O_3	1,21	1,19	0,92
FeO	3,10	2,40	1,21
MnO	0,08	0,05	0,02
MgO	1,53	1,05	0,62
CaO	3,43	2,19	1,24
Na_2O	4,76	3,47	3,02
K_2O	1,79	4,49	4,82
P_2O_5	0,19	0,20	0,07
H_2O	1,10	0,82	0,52
Total	100,36	100,32	99,81
U—$n \cdot 10^{-4}$%	1,2	5.7	9,3
Th—$n \cdot 10^{-3}$%	0,5	3,3	9,7
Th/U	4,1	5,8	10,4

Note: Comma represents decimal point.

I. THE OLDEST GRANODIORITE AND PLAGIOGRANITES

The granodiorites and plagiogranites are the oldest granitoids of the middle Dnepr region. Their origin is related to the folding and regional metamorphism of the oldest volcanic-sedimentary series forming the first stratigraphic unit of the region [3, 4]. Their pre-Krivoi Rog age is proved by the fact that the basal beds of the Krivoi Rog metamorphic series overlie the plagiogranites of the Saksagan' River and by the presence of plagiogranite pebbles in the conglomerates of the series [5]. According to determinations by the argon method, the age of the plagiogranites is over 2100 million years [6]. The most recent age determinations give values up to 3000 million years for some of the granodiorite masses occurring among the Dnepr region migmatites.

The granodiorites and plagiogranites occur in a series of rather small massifs (from 10 to 100 km^2) along the banks of the Dnepr and on the Mokraya Sura and Saksagan' rivers among the migmatites, gneisses, and amphibolite of the oldest metamorphic suite. To this series belong the massifs near Kremenchug, Dneprodzerzhinsk, and Dnepropetrovsk on the Mokraya Sura River, near Zaporosh'e and near Krivoi Rog.

The granodiorites and plagiogranites are evidently palingenetic, formed by the fusion of the volcanic-sedimentary series. The dominant rocks of the enclosing metamorphic suite are migmatites occupying an area many hundreds of times as great as the area of the granitoids. The migmatites do not occur as aureoles around the granitoid bodies, but have a wide areal distribution. They cannot, therefore, be ascribed to contact metamorphism. More probably they were formed by selective fusion of the volcanic sedimentary series. Locally, complete melting of these rocks might have resulted in the formation of considerable masses of homogeneous granitic material which, under the influence of tectonic movement, migrated into the zones of lower pressure and crystallized, there forming bodies of intrusive aspect. The fact that the granitic material in the migmatites is mineralogically and chemically identical with the plagiogranites speaks for this hypothesis. The hypothesis of palingenetic origin of the granodiorites and plagiogranites was advanced by V. I. Luchitskii [7]. The very important role of ultrametamorphism in the formation of the Precambrian granitoids is stressed in the works of N. G. Sudovikov [8, 9].

The granodiorites and plagiogranites are massive, less commonly gneissoid, rocks with medium- or coarse-grained texture. They are composed of plagioclase (60-65%), quartz (30%), and biotite (5-10%). Hornblende is sometimes found in the granodiorites. The accessory minerals include magnetite, pyrite, apatite, sphene, zircon, and allanite. Sphene and allanite are very characteristic minerals for this group of rocks although they are not quantitatively predominant. The secondary minerals in these rocks are quartz, albite, epidote, chlorite, sericite, and limonite.

The characteristic feature of the chemical composition of the granitoids of this complex (Table 1) is the strong predominance of sodium over potassium content is reflected in the mineralogy of the rocks. They are almost devoid of potassium feldspars.

The numerous measurements of gamma activity of the granodiorites and plagiogranites from six massifs gave very low values ranging from 1 to 6 γ, or 4 γ on the average, thus indicating a very low content of the radioactive elements (K^{40}, U, and Th).

The radiochemical analysis of 14 mixed samples of granitoids from the six massifs showed the following variations in the uranium and thorium content: uranium, from 0.6 ppm to 2.1 ppm, or an average of 1.2 ppm; thorium, from 3 to 9, or an average of 5 ppm; the Th/U ratio is 4.1.

The data given above show that about 30% of uranium and thorium occurs in biotite and in the heavy mineral fraction. The larger part of uranium and thorium remains in the quartz-feldspar fraction because of the imperfect separation of the accessory minerals, or possibly because a part of the uranium and thorium is dispersed in the essential minerals.

II. THE GRANITES OF THE KIROVOGRAD-ZHITOMIR COMPLEX

The granites of this complex are the most widespread in the Ukraine.

Table 2

Distribution of Uranium and Thorium Among the Mineral Fractions in Plagiogranite (samples 1408, 1419)

Fraction	Content in the fraction, %	Percent of the total content in rock	
		U	Th
Quartz-feldspar, sp. g. <2.9	90.1	70.2	69.4
Fraction with sp. g. 2.9-3.3	9.5	26.8	26.6
Fraction with sp. g. >3.3	0.4	3.4	3.8

Over 40% of the area occupied by the granitoids is composed of the Kirovograd-Zhitomir granites. The complex contains the following rocks:

1. The porphyritic granites of the Kirovograd type and the red trachytoid granites.
2. The gray medium-grained granites of the Zhitomir type.

That these granites are genetically related is proved by their occurrence together in the zoned plutons and by the presence of transitional rocks. These granites were formed during the principal (Saksagan') phase of folding and regional metamorphism of the Krivoi Rog series [3]. This is confirmed by their absolute age of 1900 to 2000 million years [6].

Investigators who have studied the petrology of the Kirovograd-Zhitomir granites [11] regard these granites as magmatic intrusive rocks formed by crystallization of a melt. We have not enough evidence on hand to deny the magmatic origin of the granites. But it should be mentioned that some of them are obviously metasomatic and not magmatic (the porphyroblastic Savro granites with relict structures in the region of Bobrints, and others). The emplacement of the granites of this complex was undoubtedly accompanied by widespread metasomatism and granitization.

In the middle Dnepr region, the granites of the Zhitomir type include those of the Ekaterinovsk and Kamensk massifs on the Kamenka River and a number of small linear massifs on the watershed of the Ingul'ts and Ingula rivers. The porphyritic granites of the Kirovograd type are represented by the Kirovograd-Bobrinets, Dolinsk, Taburishchensk (on the Dnepr), Sofievka, Sergeevka (on the Saksagan' River) and B. Rekalova River granites. Most of the granites of the Kirovograd-Zhitomir complex outcrop outside of our region.

Our geochemical studies included all of the larger Kirovograd-Zhitomir granitic massifs of the Ukraine. The results of these studies were published in a separate paper [1] and only a summary of the data will be given here.

The two types of granites of the complex are very similar in composition but differ in texture. The granites of the Zhitomir type are equigranular and medium-grained, while those of the Kirovograd type are porphyritic and coarse-grained. Both types of granites are usually gray. They are composed of approximately equal amounts of microcline perthite and plagioclase (60 - 70%), quartz (30 - 35%) and biotite (1 - 5%). Besides the biotite granites, there are amphibole-biotite and muscovite-biotite granites, but they occupy a subordinate position.

The granites of this complex are characterized by the presence of the following accessory minerals: almandine, magnetite, ilmenite, apatite, zircon, monazite, rutile, and sometimes tourmaline. The amphibole-biotite granites of the Dolinsk massif and the Saltychei Mogila (Azov region) contain sphene and allanite but no monazite. The muscovite-biotite granites contain dark zircon and thorite. The most characteristic accessory minerals in the rocks of the complex are the ever present almandine and monazite. Characteristic also is the complete absence of fluorite.

Our investigations show that monazite has a regional distribution in the porphyritic granites of the Kirovograd type. The more acid potassium-rich granites have the highest monazite content. The monazites of the Kirovograd granites differ in morphology, uranium and thorium content and Th/U ratio from the accessory monazites of the granitoids of the other Ukrainian complex (Table 3), and this completes the specific geochemical characteristic of these granites.

Table 3

Uranium and Thorium Content in the Accessory Monazites of the Ukrainian Granites [12, 13]

Source of monazite	Number of samples	Content, %		Th/U
		U	Th	
Monazite from the black-quartz granites (Tokovskii complex). Age 1700-1800 million years	6	0.27	10.26	38.0
Monazite from porphyritic granites of the Kirovograd-Zhitomir complex. Age 1900-2000 million years	15	0.42	7.29	17.3
Monazite from read charnockite granites of Pobuzh'e. Age 1950 million years	8	0.09	9.76	108.4
Monazite from the Chudnovo-Berdichev granites. Age 2100 million years	6	0.67	4.59	6.8

Unlike the granitoids of the oldest complex, which are sodic, the Kirovograd-Zhitomir granites are potassium-sodium rocks with potassium predominating (K_2O:Na_2O -- 1 :3). Their potassium and magnesium content is two-thirds of that in the plagiogranites (see Table 1).

The measurements of the gamma activity and determinations of uranium and thorium in the Kirovograd-Zhitomir granites from twenty Ukrainian complexes are given in a generalized form in Table 4 and Figs. 1, 2 and 4.

The data of Table 4 show clearly that the two types of granites of the

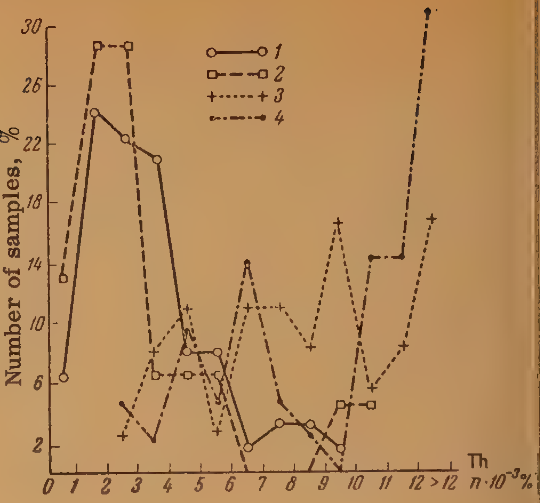

Fig. 1. Distribution of thorium in the granites of the Kirovograd-Zhitomir and Tokovskii complexes

1 -- porphyritic granites of the Kirovograd type (62 samples); 2 -- medium-grained granites of the Zhitomir type (38 samples); 3 -- porphyritic granites of the Tokovskii complex (37 samples); 4 -- dike granites of Tokovskii complex (43 samples)

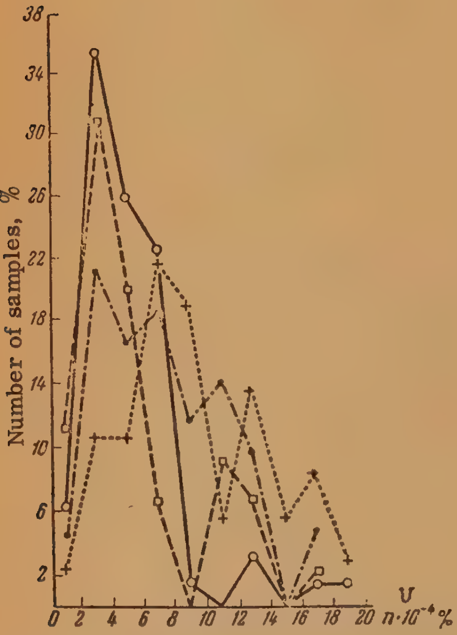

Fig. 2. Distribution of uranium in the granites of the Kirovograd-Zhitomir and Tokovskii complexes (symbols as in Fig. 1)

Kirovograd-Zhitomir complex have very similar gamma activity and uranium and thorium content and that each type is sharply divided into two groups:

1) unaltered biotite granites and

2) muscovitized (muscovite-biotite) granites.

Radiochemical analysis of 100 samples of the granites of this complex gave 5.7 ppm as the average uranium content, which is near the clarke for granites [1], and a high thorium content of 33 ppm. The Th/U ratio is 5.8. There is a definite relation between the uranium and thorium content and the composition of the rocks, and the effect of the postmagmatic processes on the redistribution of the radioactive elements is quite clear.

The biotite granites which did not undergo postmagmatic changes (muscovitization and silicification) show gamma activity normal for granites and contain, on the average (75 samples analyzed), 4.5 ppm uranium and 25 ppm thorium, with the Th/U ratio = 5.5. The more basic varieties of the amphibole-biotite

Table 4

Average Uranium and Thorium Content in the Granites of the Kirovograd-Zhitomir Complex

Type of granite	Gamma activity, units	Number of samples	Content		Th/U
			$U \cdot 10^{-4}\%$	$Th \cdot 10^{-3}\%$	
Biotite granites					
Porphyritic	18–20	46	4.2	3.6	6.2
Medium-grained	18–20	30	5.1	2.3	4.5
Muscovitized (muscovite-biotite) granites					
Porphyritic	20–88	16	8.4	5.3	6.3
Medium-grained	20–88	8	10.5	6.1	5.8
Average		100	5.7	3.1	5.8

granites containing sphene and allanite are the poorest in uranium and thorium. The acid potassium-rich granites containing monazite have a relatively high thorium content and a normal or somewhat higher than normal uranium content.

The gamma activity and uranium and throium content of the muscovitized muscovite-biotite granites are twice as high as in the biotite granites. The muscovite-biotite granites of the Polonnaya station, the Novo Romanovsk quarry (Podolia), the town of Korostyshev and the village of Kurchitsa (on the Sluch' River) contain zircon, monazite, and thorite. The average content of uranium (24 samples) in these rocks is 9.1 ppm and of thorium, 56 ppm; the Th/U ratio is 6.1.

In the zoned Yantsev massif (Zaporozh'e), composed of the Zhitomir type of granites, uranium has accumulated in preference to thorium in the peripheral zone of the massif composed of albitized and silicified pegmatoidal and aplitic granites.

	U (ppm)	Th (ppm)	Th/U
Granites of the central part of the massif	5.4	48	8.9
Granites of the peripheral zone of the massif	9.9	24	2.4

These data show clearly the effect of postmagmatic processes on the redistribution of radioactive elements.

III. THE GRANITES OF THE TOKOVSKII COMPLEX

The red microcline alaskites of the Tokovskii complex are the youngest granites of the Middle Dnepr region. They cut the gray Kirovograd-Zhitomir granites and the Krivoi Rog metamorphic series. They were emplaced during the second epoch of folding (Demurinsk) of the Krivoi Rog series and caused alkali metasomatism of its rocks [10]. The absolute age of the granite complex measured by the lead isotope and argon methods is 1700-1800 million years [6]. They are evidently synchronous with the Korosten granites of Volynia.

The Tokovskii complex consists of:

1) the red alaskites of the Tokovskii massif and their dike rocks, the fine-grained granites on the Saksagan' River and the right bank of the Dnepr and 2) the red granites with black quartz of the Ingul'ts River region.

The average chemical composition of the granites of this complex given in Table 1 shows that they are alaskites, i. e. have a high silica and alkali content with a strong predominance of potassium over sodium and a low calcium and magnesium content.

1. The Tokovskii granites

The alaskites of the Tokovskii massif and their derivatives are of especial geochemical interest. Our earlier investigations [14] showed that they have strong gamma activity and are enriched in the radioactive elements, especially thorium. The granites are thorium-bearing on a regional scale. They are responsible for the postmagmatic processes which affected the granites themselves and the metamorphic rocks of the Krivoi Rog series. The metasomatic rocks are characterized by preferential concentration of uranium.

The Tokovskii massif granites (on the Kamenka and Bazavluk rivers) are red porphyritic and coarse-grained. They are composed of microcline perthite (up to 40%), sodic plagioclase (25-30%) and quartz (35-40%). Their biotite content is very small (1-2%).

The accessory minerals are magnetite, apatite, sphene, dark zircon in stubby prisms, thorite, molybdenite, pyrite, and hematite. Fluorite is occasionally present. Thorite, dark zircon, and molybdenite are the distinctive minerals among the accessories of the Tokovskii granites. The accessory thorite in the granites and their derivatives is represented by three varieties: thorite, phosphothorite, and uranothorite, which were described by us earlier [15]. The pegmatites contain in addition allanite, and the dike granites xenotime.

The measurements of the gamma activity and the determinations of uranium and thorium content in the granites of the Tokovskii massif (48 samples) given in Table 5 show strong gamma activity, strong enrichment in thorium, and a relatively high uranium content. The thorium content ranges from 41 to 171 and averages 96 ppm, which is four times as high as its clarke in granites [16]. The content of uranium varies from 2.4 to 18.9 average 9.6 ppm and in most samples exceeds the clarke value. The average Th/U ratio is 10.0.

The aplites and aplite-pegmatites of the massif are characterized by a large variation in the content of uranium and thorium (see Table 5), owing to the irregular distribution of the radioactive accessory minerals. In the areas of concentration of thorite, malacon, and allanite, the uranium and thorium content is high.

The metasomatic zoisite-albite-quartz rocks formed by the replacement

Table 5

Uranium and Thorium Content in Granites and Aplite-Pegmatites of the Tokovskii Complex
(Data of the Laboratory of Geochemistry of Rare Elements, Radium Institute, Academy of Sciences USSR)

Rock	Gamma activity, units	Number of samples	Content		Th/U
			$U \cdot 10^{-4}\%$	$Th \cdot 10^{-3}\%$	
Porphyritic granites, Tokovskii massif	32	31	9.6	9.6	10.0
Aplite-pegmatites, Tokovskii massif	high >50	13	2.1–36.0	4.1–79.0	4.0–28.3
Fine-grained dike granites of the Saksagan' River type	50	21	9.6	13.7	14.2
Aplite-pegmatites of the Saksagan' River region	high >50	10	3.3–48.3	3.0–87.3	10.0–72.0
Fine-grained dike granites of the villages of Mishurin Rog and on the Dnepr	33	7	8.4	7.1	8.4
Porphyritic black-quartz granites of the Ingul'ts River region	19	6	6.9	3.7	5.3
Fine-grained aplitic black-quartz granites of the Ingul'ts River region	24	15	4.5	6.8	15.1
Average for all rocks of the complex except two samples of strongly enriched samples of aplite-pegmatite		101	9.3	9.6	10.4

of the porphyritic Tokovskii granites contain, on the average (5 samples), 26.1 ppm of uranium and 142 ppm of thorium, the Th/U ratio being 5.4. These rocks contain allanite, sphene, malacon, phosphothorite, and uranium-bearing epidote.

The radiochemical analysis of the mineral fractions of the Tovoskii granites shows that uranium and thorium in these rocks occur almost entirely in the accessory minerals, the main concentrators being thorite (phosphothorite) and zircon. Over 90% of thorium and 80% of uranium in the granites occur in the acid-soluble form, mainly in thorite.

In the middle course of the Saksagan' River, within the sublatitudinal Demurinskii anticlinorium, there are veins of red fine-grained granites and aplite-pegmatites. Their composition, accessory minerals, and content of radioactive elements are identical with the Tokovskii granites and are obviously genetically related to them. The dike granites and aplite-pegmatites show strong gamma activity (Table 5), contain accessory thorite and phosphothorite, molybdenite, and dark zircon (malacon). Their thorium content is even higher than in the porphyritic Tokovskii granites, and averages 137 ppm; the uranium content is 9.6 ppm and the Th/U ratio = 14.2. The aplite-pegmatites show a considerable variation in the uranium and thorium content, which may be quite high (Table 5). As in the Tokovskii granites, the main concentrators of uranium and thorium in the dike granites are thorite, phosphothorite, and zircon (malacon). A study of phosphothorite from the aplite-pegmatite on the Saksagan River showed that it is a hydrated silico-phosphate of thorium and iron similar in composition and properties to the mineral smirnovite [15].

Similar to these dike granites are the red thorium-bearing subalkalic microgranites of the right bank of the Dnepr. They also are enriched in thorium for their average thorium content is 71 ppm, with the uranium content being 8.4 ppm (seven samples from 5 dikes).

Genetically related to the intrusion of the thorium-bearing Tokovskii granites are the metasomatites (albitites, aegirinites) of the Krivoi Rog series formed as a result of the alkali metasomatism of schists [10]. The radiochemical analysis of eight samples of the metasomatites shows preferential accumulation of uranium and a thorium content up to 94 ppm. Such high thorium content in the metasomatites formed from the Krivoi Rog schists, which are very poor in thorium (< 5 ppm), indicates a genetic relationship between the metasomatites and the derivatives of the Tokovskii granites strongly enriched in this element. Among the accessory minerals of the metasomatites, malacon is abundant and thorite, characteristic of the Tokovskii granites, is occasionally found.

The comparison of the radiochemical data for the Tokovskii granites and for their derivatives given in Fig. 3 shows a perfectly definite dependence of the distribution and of the behavior of uranium and thorium on the stages of the geological process. From the orthomagmatic to the pegmatitic stage, there was a preferential accumulation of thorium. The Th/U ratio increased and reached its maximum in the pegmatites. In passing to the postmagmatic stage, a sharp change occurred in the behavior of uranium and thorium. The uranium content grew rapidly and that of thorium diminished from the pegmatites to the hydrothermal, metasomatic, and dike rocks.

2. The Black Quartz Granites

The black quartz granites are found on the Ingul'ts River and on its right

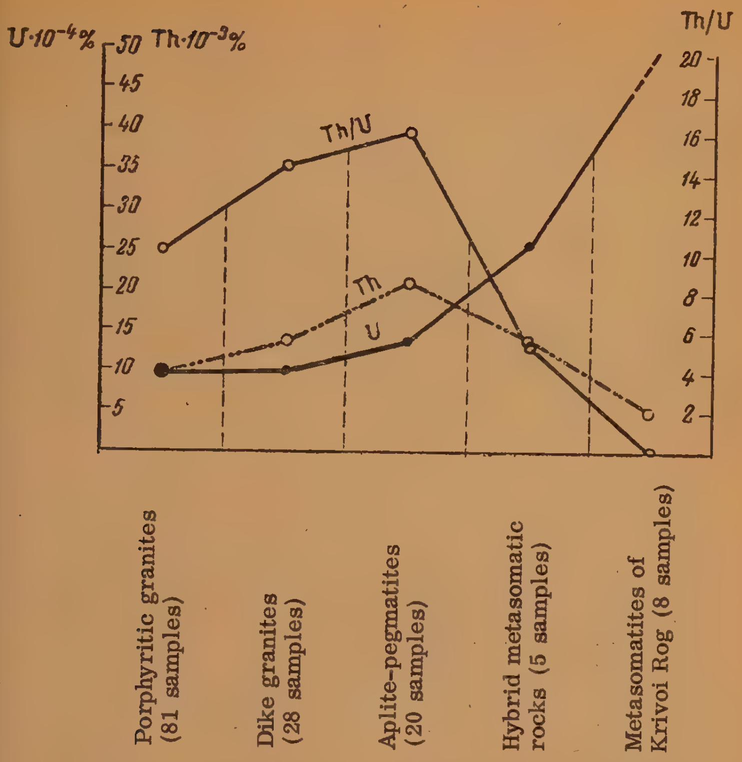

Fig. 3. Uranium and thorium content in the thorium-bearing Tokovskii granites and their derivatives

land tributaries. They form three massifs: Bokovyanskii (near the village f Bratolyubovka), Spasovskii (on the Verblyuzhka River), and Inguletskii. he dominant rock type is red coarse-grained porphyritic granite forming he central parts of the massifs. The black quartz granites were formed rom palyngenetic magma contaminated by assimilation at depth of the py-oxene-amphibole-plagioclase gneiss [11]. This explains why these gran- es have a different mineralogical composition and a different accessory ineral assemblage than the Tokovskii granites.

They are composed of microcline perthite (35-40%), plagioclase (25-0%), black quartz (40%), and biotite (3-5%). Sometimes they contain ornblende and hypersthene. Of the accessory minerals, the following have een observed: magnetite, apatite, ilmenite, pyrite, zircon, monazite, arnet, rutile, and molybdenite. Fluorite is rare. Thus, the accessory ineral assemblage is similar in part to that in the Tokovskii and the irovograd-Zhitomir granites.

The monazite of the black quartz granites is quite different morphologi-lly and in its uranium and thorium content from the monazite of the rovograd granites (see Table 3). The presence of dark stubby zircon crystals, molybdenite, and occasional fluorite, and the high thorium content in the black quartz granites reflect the geochemical characteristics of the Tokovskii granites.

The gamma activity and the uranium and thorium content were measured on samples from the Bratolyubovskii and Spasovskii massifs. The results are given in Table 5. The porphyritic granites gave the following averages: uranium 6.9 ppm and thorium 37 ppm, the Th/U ratio being 5.4. The fine-grained aplitic granites are even richer in thorium. Their average thorium content is 68 ppm, while the uranium content is somewhat lower than the clarke value and amounts to 4.5 ppm. The Th/U ratio equals 14.1. The high thorium content is due to the accumulation of thorium-rich monazite. The black quartz granites are monazite-bearing on a regional scale.

The average content of the radioactive elements in the rocks of the Tokovskii complex, as shown by the analysis of 101 samples (not counting two strongly enriched samples of aplite pegmatite) is 9.3 ppm U and 97 ppm Th, with a Th/U ratio of 10.4 being the highest among the granitoids of the other complexes (see Table 6 and Figs. 1, 2 and 4).

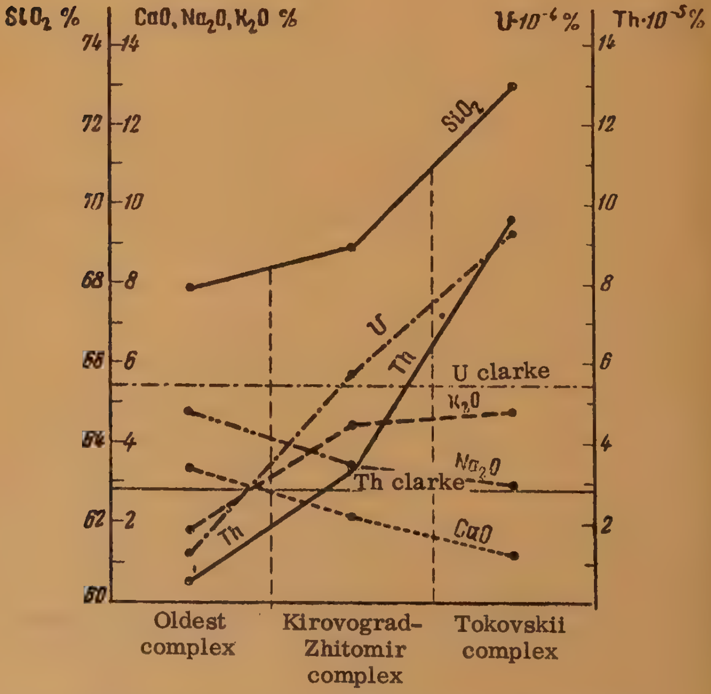

Fig. 4. Dependence of U and Th content on the chemical composition of the granitoids of the middle Dnepr region (U and Th clarkes in granites after L. V. Komlev [14])

Table 6

Average Uranium and Thorium Content in the Granitoids of the Middle Dnepr Region

Complex	Number of samples	Content, %		Th/U
		$U \cdot 10^{-4}$%	$Th \cdot 10^{-3}$%	
The oldest complex	14	1.2	0.5	4.1
Kirovograd-Zhitomir complex	100	5.7	3.3	5.8
Tokovskii complex	101	9.3	9.7	10.4

Summary

1. In the Middle Dnepr region there are three granitoid complexes different in age, composition, and geochemical characteristics. The evolution in the composition of the granitoids of the three complexes from the older to the younger consisted in the decrease in the sodium, calcium, and magnesium content and increase in the content of potassium, silica, the radioactive elements, uranium, and thorium.

2. The granitoids of the oldest complex, granodiorites and plagiogranites, contain the least amounts of uranium and thorium, one-fourth the clarkes of these elements in granites and in this respect they resemble the enclosing metamorphic rocks.

3. The granites of the second, Kirovograd-Zhitomir complex, have uranium contents approximating the clarke, and thorium contents higher than the clarke.

4. The third, Tokovskii complex of microcline alaskites, is strongly enriched in the radioactive elements, especially thorium. The uranium content of its rocks is almost twice as high as the clarke, and the thorium content four times as high as the clarke. These rocks have the highest uranium and thorium content of all the Ukrainian granitoids.

5. The data presented here confirm the face of progressive concentration of the radioactive elements with decreasing age in the three granitoid complexes of the Middle Dnepr region. This important geochemical phenomenon had already been noted by one of the authors [16].

6. According to their content of the most characteristic accessory minerals, the granitoids of the Middle Dnepr region are divisible into three types:

a) the allanite-sphene type, which includes the granodiorites and plagiogranites of the oldest complex and the amphibole-biotite varieties of the Kirovograd-Zhitomir granites;

b) the monazite-garnet type, which includes the biotite granites of the Kirovograd-Zhitomir complex and the black quartz granites of the Ingul'ts River region;

c) the thorite-molybdenite type, represented by the Tokovskii granites.

7. The allanite-sphene granites are the poorest in the radioactive elements. Uranium and thorium in these rocks are partially concentrated in

the accessory minerals: zircon, sphene, epidote, apatite, and allanite. A part of these elements is present, apparently in the dispersed state, in the essential minerals. The monazite-bearing granites are definitely thorium-bearing. Their high thorium content is due to the accumulation of the accessory monazite. Monazite and zircon are the main concentrators of uranium and thorium in granites of this type. The thorium-bearing granites are still more pronouncedly thorium-bearing rocks, but they also have a relatively high uranium content. Uranium and thorium in these granites are concentrated almost entirely in the accessory minerals, with thorite and zircon carrying 90% of the total content of these elements.

8. The geochemical data obtained during the study of the granitoids of the Middle Dnepr region confirm the truth of the previously established geochemical regularities of distribution of uranium and thorium, i. e. their preferential concentration in the acid alkali-rich granitoids, the progressive concentration of these elements in the end products of the differentiation of granitic magma, the sharp change in the behavior of uranium and thorium in passing from the orthomagmatic to the postmagmatic stage and the important role of the postmagmatic alteration of the rocks in the redistribution of the radioactive elements.

9. It has been established that the Tokovskii granites and their derivatives are enriched in thorium on a regional scale and that there are three varieties of thorite: thorite, phosphothorite, and uranothorite, among their accessory minerals.

10. The totality of the obtained data, on the uranium and thorium content in granites, on the characteristic assemblages of accessory minerals and on the minerals carrying radioactive elements, is a substantial contribution to the general geological-petrographic characteristic of the granitoids of the middle Dnepr region and may be useful in the study of the metallogeny of the Ukrainian Precambrian.

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GALLIUM IN THE ROCKS OF THE LOVOZERO ALKALI MASSIF

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The data in the literature on the distribution of gallium in the nepheline-bearing rocks have been based mainly on the figures published by Goldschmidt and Peters [1]. According to these figures, nepheline rocks contain 0.005% Ga_2O_3 (average of 8 analyses) and their $Ga_2O_3:Al_2O_3$ ratio is 1:4000. According to Gordon and Murata [2], the Arkansas nepheline syenites contain 0.002% Ga (average of three analyses).

Recently Borisenok [3] compiled data on the distribution of gallium in the rocks of the Soviet Union. According to these data the alkalic rocks (nepheline syenites, syenites, monzonites, and shonkinites) contain from 0.0018 to 0.0070% Ga, or 0.0040% on the average. The $Ga/Al \cdot 10^4$ ratio in these rocks ranges from 3.0 to 5.6 and averages 4.1.

The present paper reviews the distribution of gallium in the rocks of the Lovozero massif (Kola Peninsula), whose area is about 530 km^2. The massif was formed in four intrusive phases. The first phase includes equigranular, porphyritic, poikilitic, and other nepheline syenites. The second phase includes urtites, foyaites, and lujavrites. The third phase is composed of eudialyte lujavrites, porphyritic lujavrites, poikilitic sodalite syenites, and tawites genetically related to them. The fourth phase is a dike complex of tinguaites, monchiquites, etc.

The bulk of the massif consists of rocks of the second and third intrusive phases. The rocks of the second phase form the base of the massif and are about 1.4 km thick, while the rocks of the third phase form its upper part and are from 150 to 450 m in thickness.

The results of our investigation of gallium and aluminum content in the rocks of the Lovozero massif are presented in Table 1, and of the gallium content in the minerals of the massif, in Table 2.

Gallium content in rocks and minerals was determined by the method proposed by Onishi and Sandell and perfected by V. S. Saltykova and E. A. Fabrikova [4]. It permits determinations of small amounts of gallium (0.0001-0.1%) in rocks and minerals by extraction of chlorgallate rhodamine B with a mixture of one volume of ether and three volumes of benzol without preliminary separation of associated elements. The method is

Gallium and Aluminum Content in the Rocks of the Lovozero Massif

Sample No.	Rock	Locality	Ga, % · 10^{-3}		Al, % chem. anal.	Ga/Al · 10^{-4}
			chem. anal.	spectr. anal.		
		Rocks of the first intrusive phase				
139	Equigranular nepheline syenite	Mt. Ninchurt	-	4.1	10.63	3.86
69	" " "	"	4.0	4.8	-	-
183	Porphyritic nepheline syenite	Mt. Alluaiv	5.0	5.8	10.92	4.57; 5.31
185a	" " "	"	4.5	5.2	-	-
193	" " "	"	4.5	4.8	-	-
66	Poikilitic nepheline syenite	Mt. Susluaiv	4.0	4.3	11.37	3.52; 3.78
431	" " "	Tavaiok river	3.0	3.4	-	-
188a	" " "	Mt. Alluaiv	4.0	3.7	-	-
196	Poikilitic nepheline syenite with hydrosodalite	" "	4.0	3.6	11.20	3.57; 2.68
		Rocks of the second intrusive phase				
276	Urtite	Mt. Alluaiv	8.0	7.7	-	-
132	Ijolite-urtite	"	8.0	8.0	-	-
145	" "	Mt. Karnasurt	9.0	-	13.72	6.56
187	" "	Mt. Alluaiv	10.0	10.0	14.24	7.02; 7.02
143	Foyaite	Mt. Karnasurt	7.5	7.0	10.11	7.91; 7.06
144	"	"	-	7.6	9.87	7.7
182b	"	Mt. Alluaiv	7.0	6.7	-	-
272	"	"	6.0	6.0	-	-
130	"	"	7.0	5.8	-	-
26b	Leucocratic lujavrite	Mt. Karnasurt	7.0	5.0	10.62	6.57; 4.70

Table 1 (Continued)

Sample No.	Rock	Locality	Ga, % · 10^{-3} chem. anal.	Ga, % · 10^{-3} spectr. anal.	Al, % chem. anal.	Ga/Al · 10^{-4}
26	Mesocratic lujavrite	Mt. Karnasurt	6.0	6.3	8.37	7.18; 7.52
27	Melanocratic lujavrite	"	5.0	4.0	8.37	5.96; 4.78
8	Amphibole lujavrite	"	4.9	4.7	7.15	6.92; 6.58
124	" "	Mt. Alluaiv	4.0	5.6	-	-
19	" "	Mt. Karnasurt	4.0	7.5	-	-
362	Lujavrite with loparite	Mt. Parguaiv	5.0	5.8	-	-
264	" "	Mt. Alluaiv	5.0	5.4	7.08	7.06; 7.64
190	Lujavrite with loparite and eudialyte	"	5.0	5.6	-	-
262	Urtite with loparite	"	8.0	7.0	11.30	7.08; 6.20
363	" "	Mt. Parguaiv	6.0	5.2	-	-
268	Urtite with loparite and apatite	Mt. Alluaiv	5.5	7.0	9.93	5.54
XIX	" " "	Mt. Kuftn'yun	7.0	5.0	-	-
1367	Malignite with loparite	Mt. Karnasurt	3.5	3.8	6.06	5.78; 6.27
		Rocks of the third intrusive phase				
160	Eudialyte lujavrite	Mt. Alluaiv	6.0	6.0	8.37	7.16; 7.16
245	" "	"	5.0	5.5	9.03	6.22; 6.86
168a	" "	"	5.0	7.5	-	-
168b	" "	"	6.0	7.2	-	-
263	Porphyritic lujavrite with lovozerite	Mt. Karnasurt	6.0	8.2	6.50	9.25; 12.61
106	" "	Mt. Vavenbed	8.0	7.9	6.46	12.38; 12.22
XXI	Porphyritic lujavrite with murmanite	Mt. Flora	7.0	6.5	8.18	8.56; 7.94

Table 1 (Continued)

Sample No.	Rock	Locality	Ga, % · 10^{-3}		Al, % chem. anal.	Ga/Al · 10^{-4}
			chem. anal.	spectr. anal.		
249	Porphyritic lujavrite with murmanite	Mt. Alluaiv	7.0	6.6	-	-
170	Porphyritic lujavrite	"	7.0	10.0	-	-
246	Porphyritic juvite with loparite	"	7.0	7.2	10.42	6.71; 6.20
141	Poikilitic sodalite syenite	Chinglusuai river	6.0	5.8	10.12	5.91; 5.73
266	" "	Tulbn'nuai river	6.0	10.0	11.18	5.37
92	" "	Uel'kuai river	7.0	7.0	-	-
430	Tawite	Tavaisk river	8.0	7.8	11.33	7.06; 6.88
110	Eudialyte rock	Mt. Vavenbed	3.0	3.8	-	-
		Rocks of the fourth intrusive phase				
1393	Monchiquite	Mt. Karnasurt	3.0	3.0	-	-
XXII	"	Mt. Alluaiv	2.0	1.9	-	-

Table 2

Gallium Content in the Minerals of the Lovozero Massif

No. of sample	Mineral	Ga, $\% \cdot 10^{-3}$			
		Pegmatite		Parent rock	
		chem. anal.	spectr. anal.	chem. anal.	spectr. anal.
1498	Nepheline	11.5	-	-	-
1531	"	12.0	-	-	-
1170	"	-	14.0	-	-
815	"	-	-	7.0	-
-	Sodalite	-	27.0	-	-
1018	"	31.0	30.0	-	-
1322	"	10.0	-	-	-
-	Ussingite	10.0	10.6	-	-
1025	Natrolite	20.0	19.1	-	-
-	"	11.0	7.0	-	-
1119	Albite	5.0	4.6	-	-
1246	"	-	8.0	-	-
1276	"	11.5	11.0	-	-
1288	Li-bearing mica	11.0	26.5	-	-
1084	Biotite	5.0	-	-	-
1286	Microcline	-	8.8	-	-
1592	"	7.0	-	-	-
138/2	"	5.0	-	-	-
1202	"	-	7.0	-	-
XVIII	"	-	-	4.0	-
XII	"	-	-	6.0	-
1493	Aegirine	5.0	-	-	-
1187	"	4.0	-	-	-
XVIII	"	-	-	3.0	3.2
XII	"	-	-	2.0	-
245	"	-	-	2.4	-
-	Aegirine (from malignite)	-	-	4.0	-
1236	Arfvedsonite	2.25	2.5	-	-
1322	"	2.0	5.0	-	-
243a	Eudialyte	0.5	-	-	-
1289	Lomonosovite	0.6	0.6	-	-
1289	Murmanite	-	0.3	-	-
1289	Lamprophyllite	<0.5	not detected	-	-
1289	Belyankinite	-	2.0	-	-
1020	Epididymite	-	0.5	-	-
-	Na-opal	-	0.2	-	-
1104	Ramsayite	-	0.3	-	-
217/3	Catapleiite	-	0.4	-	-
1395	Loparite	-	none	-	-

accurate within 10-15%.

The data on the gallium content obtained by the rhodamine method were compared with the results obtained spectrographically by the method developed by Borisenok [5].

The results of determinations, given in Table 1, show that the amount of gallium in the rocks of the massif ranges from 30 to 100 ppm. The average content in the rocks of the first intrusive phase is about 41 ppm and in the second and third phases, about 60 ppm. If it is taken into consideration that the rocks of the first intrusive phase constitute no more than 2% of the total volume of the massif and the rocks of the second and third phases, about 98%, the total gallium content in the massif is 60 ppm. This is higher than the average for nepheline syenites cited in the works of Borisenko 40 ppm [3] and Goldschmidt--38.5 ppm [1].

The Ga/Al $\cdot$ 10^{-4} ratio in the Lovozero rocks ranges from 3.5 to 12.4. In the rocks of the first intrusive phase, it is from 3.5 to 4.5, in the rocks of the second phase, 5.5 to 7.91, and in the rocks of the third phase, 5.4 to 12.4. These figures are considerably higher than the figures given by Borisenko for the nepheline syenites of other regions of the Soviet Union.

In the Lovozero nepheline syenites, the lowest values of the gallium-aluminum ratio (3.5 - 4.6) were obtained for the rocks of the first intrusive phase and the highest (5.4 - 12.4) for the rocks of the third phase. The maximum values of the ratio (8.56 - 12.38) in the rocks of the third intrusive phase were found in the porphyritic lujavrites, which were formed later than the eudialyte lujavrites. This indicates that gallium accumulates towards the end of the magmatic process and is confirmed by the data of Table 2. For example, gallium content in aegirine, microcline, and nepheline in the pegmatites is higher than in the same minerals of the parent rocks.

In the Lovozero massif, gallium is associated mainly with aluminum, as can be seen from the data of Table 2. However, the concentration of gallium in the rocks of the massif is not proportional to the aluminum content (see Fig. 1). If such a relation existed the gallium-aluminum ratio would

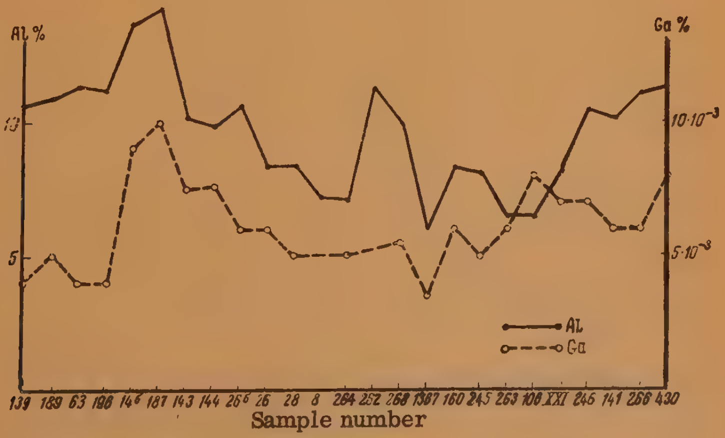

Fig. 1. Aluminum and gallium content in the rocks of the Lovozero massif

be constant. In reality, it varies quite considerably, from 3.5 to 12.4. This is explained by the fact that in the minerals, gallium substitutes diadochically not only for aluminum ($Al^{3+} = 0.57$ A, $Ga^{3+} = 0.62$ A) but also for ferric iron ($Fe^{3+} = 0.67$ A) in aegirine and arfvedsonite, as show by the data of Table 2. Aegirine, which is an essential mineral in most of the rocks of the massif, contains from 20 to 40 ppm Ga, and this is half its content in the K-Na feldspar (microcline) with 40 to 60 ppm Ga. The rathe high gallium content in the minerals of the Lovozero massif had already been noted by one of the authors of the present paper [6].

In the titano- and zirconosilicates (eudialyte, lomonosovite, murmanite lamprophyllite) which do not contain aluminum and iron, the gallium conten is usually low (Table 2).

Our investigations lead to the following conclusions:

1. The gallium content and the gallium-aluminum ratio in the nepheline syenites of the Lovozero massif are higher than in the rocks of the same type in other massifs.
2. In the Lovozero massif the highest gallium-aluminum ratio is found in the rocks of the third intrusive phase, indicating that gallium is concentrated in relation to aluminum in the late stages of the magmatic process. The lowest values of the ratio and the lowest gallium content characterize the rocks of the first intrusive phase.
3. The geochemical history of gallium in the rocks of the massif parallels that of aluminum and also, in part, of the trivalent iron which gallium replaces diadochically in aegirine and other minerals.

In conclusion, the authors express their gratitude to Yu. B. Kholina for her determinations of aluminum in the rocks of the Lovozero massif.

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DISTRIBUTION OF ALKALI METALS AND THALLIUM IN THE GRANITOIDS F THE TURGOYAK PLUTON (MIDDLE URALS)

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The behavior of the rare alkalies and Tl during certain contact processes ybridism and assimilation) have not been sufficiently studied. Of con- derable interest is the determination of the pattern of distribution of the re alkalies (Li, Rb) and Tl in relation to the behavior of the common kalies (K, Na).

The Turgoyak granitic pluton (Middle Urals) is a good locality for the udy of these phenomena.

According to some investigators [1], the pluton is a granitoid stock tting through a Silurian-Devonian volcanic-sedimentary sequence. The anitoids outcrop over an area of about 65 km^2. In the west they are bor- red by quartzites metamorphosed into micaceous quartzites at the con- ct. In the southeast and northeast the pluton is bordered by a sequence of eenstones. At the contact these rocks have been chaned into amphibolites, phibole schists, and hornfelses.

The granitoids of the Turgoyak massif (except for the dike series) are presented by three varieties: 1) the leucocratic granites with a little otite, which occupy the smallest area, being restricted to the central rts of the massif and merging radually into the biotite granites; 2) the otite granites, the most abundant rocks of the pluton; and 3) the grano- rites, gradually merging into the biotite granites and occurring mainly ar the contact zones. As the contact is approached, the content of dark nerals in the granodiorites, especially of hornblende, increases ticeably.

The granodiorite zones are characterized by the presence of xenoliths d of the invaded rocks. The gradual change with approach to the con- ts from the leucocratic granites to the biotite granites and granodiorites, taxitic aspect of the rocks, the strong development of the zone of xeno- hs, the porphyritic texture of the granites, all these features, as pointed by V. S. Koptev-Dvornikov [2], who has studied hybridism in some anitic intrusions of Central Kazakhstan, indicate that the granitoids of Turgoyak pluton were formed not by magmatic differentiation but by the ion of a melt of leucocratic granite composition on the enclosing gabbros peridotites. This resulted in the formation of rocks of intermediate composition (granodiorites) enriched in Fe, Mg, and Ca derived from the enclosing rocks.

A micrometric analysis of thin sections (with an integrating stage) shows a gradual increase in the content of biotite and hornblende from leucocratic granites to granodiorites, indicating that the rocks become more basic from the center of the pluton to its periphery (Table 1).

That the rocks of the endocontact zone are enriched in iron is shown by the fact that their hornblendes and biotites have a higher iron content than the same minerals in the leucocratic granite. The iron content was determined by measuring N_g and using V. Sobolev's diagrams of the relationship between the refractive index and the iron content ([3] Table 2).

Table 1

Mineralogical Composition of the Rocks of the Turgoyak Pluton in %

Rock	Plagioclase	Quartz	Microcline	Biotite	Hornblende	Accessory minerals
Leucocratic granites	42.0	30.0	22.0	4.0	–	2.0
Biotite granites	38.6	20.4	26.0	10.5	1.0	3.5
Granodiorites	35.3	19.4	19.2	14.0	8.0	3.7

The increase in the Fe and Mg content in the endocontact rocks is accompanied by an increase in Ca content, as indicated by the fact that while in the leucocratic granites the composition of the plagioclase ranges from $\underline{An_8}$ to $\underline{An_{10}}$, in the granodiorites it is $\underline{An_{28}}$.

Table 2

Iron Content in the Different Rocks of the Turgoyak Pluton

Rock	Mineral	N_g	FeO content mol. %
Leucocratic granite	Biotite	1.647	51
Biotite granite	Biotite	1.650	55
	Hornblende	1.658	25
Granodiorite	Biotite	1.663	66
	Hornblende	1.668	36

Thin section study showed that alkali metasomatism played an important role during the formation of the Turgoyak granites. This is especially clearly seen in the biotite granites, where soda meta somatism resulted in corrosion and replacement of the earlier minerals by microcline.

To determine the behavior of the alkalies (Li, Na, K, and Rb) and of thallium in the granitoids of the Turgoyak pluton and in the enclosing rocks, samples weighing from 500 g to 1 kg were taken in the field along three profiles from the center to the contacts.

The alkalies were determined on a flame spectrophotometer under the supervision of D. N. Ivanov and V. I. Lebedev*. The samples (weighing 2 g) were treated with hydrofluoric acid containing a few drops of concentrated sulfuric acid until the silicates were completely decomposed. The dry residue was dissolved in hot 0.5N HCl, the solution filtered into a flask, and its volume brought to 100 ml. The accuracy of the method was ±5%. Thallium was determined by the method proposed by N. T. Voskresenskaya [4]. Its accuracy was ±15-17%.

The distribution of the common and rare alkalies showed the following pattern:

Potassium. The potassium content in the leucocratic granites ranges from 1.55 to 2.47% and averages 1.80% (Table 3). This figure is somewhat higher than the average potassium content in acid rocks according to A. P. Vinogradov [5]. In the biotite granites the average potassium content increases to 2.4%. In the direction of the contact, the potassium content in the rocks increases at first, but with change to the granodiorites it decreases to the average of 1.6%. In the enclosing rocks (micaceous quartzites) there is even less potassium, for at the contact with the granodiorites its content is 1.5% and 100 m to the west of the contact, only 0.8% (see Fig. 1).

Sodium. The behavior of sodium in the rocks of the Turgoyak pluton is similar to that of potassium. In the leucocratic granites the sodium content averages 3.6%, which is considerably more than the average sodium content in granites in general as given by Vinogradov [5]. In the biotite granites the sodium content reaches 4.0% and in the granodiorites it decreases to 3.4%. In the micaceous quartzites there is much less Na than K; at the granodiorite contact its content is only 0.12% and 100 m to the west of the contact, 0.08% (Table 3 and Fig. 1). The lower concentration of sodium as compared with potassium in the enclosing rocks is evidently due to the fact that much less of it is contributed by the granodiorites.

Lithium. The lithium content in the leucocratic granites shows a considerable range, from 0.0004 to 0.0018%, depending on the amount of dark minerals present in the rocks. The varieties of leucocratic granites which are enriched in Mg and Fe contain more Li. This is due to the intimate geochemical relationship between Li and Mg and Fe. The average lithium content in the leucocratic granites is 0.0012%, which is lower by one order than V. M. Goldschmidt's clarke of this element in granites [6]. In the biotite granites the lithium content is about twice as high because of an increase in the content of dark minerals. In the granodiorites the content of lithium varies little and averages 0.002%, which is lower than Goldschmidt's

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Table 3

Content of the Alkalies and Thallium in the Rocks of the Turgoyak Pluton (%)

Sample No.	Na	K	Li	Rb	Tl
			Leucocratic granites		
1	4,00	2,47	0,0004	0,008	$3,6 \cdot 10^{-5}$
2	3,50	1,71	0,0009	0,004	$5,0 \cdot 10^{-5}$
3	3,70	1,55	0,0018	0,004	$2,0 \cdot 10^{-5}$
4	3,00	1,70	0,0005	0,002	$1,5 \cdot 10^{-5}$
5	3,60	1,65	0,0018	0,006	$3,0 \cdot 10^{-5}$
6	3,70	2,10	0,0018	0,005	$3,0 \cdot 10^{-5}$
Average	3,60	1,80	0,0012	0,005	$3,0 \cdot 10^{-5}$
Average:	K/Li = 1500;	Na/Li = 3000;	Rb/Tl = 180;	Na/K = 2	
			Biotite granites		
7	3,00	2 05	0,0030	0,009	$7,0 \cdot 10^{-5}$
8	4,00	2,35	0,0025	0,011	$7,0 \cdot 10^{-5}$
9	4,20	2,15	0 0020	0,008	$6,0 \cdot 10^{-5}$
10	4,50	2,50	0,0018	0,009	$5,0 \cdot 10^{-5}$
11	4,45	2,80	0,0020	0,014	$5,5 \cdot 10^{-5}$
12	4,50	2,20	0,0021	0,012	$6,5 \cdot 10^{-5}$
13	3,70	2,00	0,0026	0,008	$8,0.10^{-5}$
14	3,50	2,30	0,0013	0,010	$7,5.10^{-5}$
15	4,50	2,85	0,0032	0,012	$1,0.10^{-4}$
16	3,90	2,90	0,0020	0,012	$8,0 \cdot 10^{-5}$
17	3,50	2,40	0,0020	0,013	$1,0 \cdot 10^{-4}$
18	3,60	2,45	0,0020	0,010	$1,0 \cdot 10^{-4}$
Average	4,00	2,40	0,0020	0,010	$7,5 \cdot 10^{-5}$
Average:	Rb/Tl = 130;	Na/K = 1,7;	Na/Li = 2000;	K/Li = 1200	
			Granodiorites		
19	3,70	2,10	0,0027	0,005	$5,0 \cdot 10^{-5}$
20	3,50	1,50	0,0020	0,004	$5,5 \cdot 10^{-5}$
21	3,30	1,50	0,0019	0,002	$2,5 \cdot 10^{-5}$
22	3,25	1,85	0,0010	0,002	$3,0 \cdot 10^{-5}$
23	3,30	1 50	0,0024	0,005	$3,5 \cdot 10^{-5}$
24	3,50	1,60	0,0020	0,003	$4,5 \cdot 10^{-5}$
25	3,45	1,70	0,0018	0,002	$4,0 \cdot 10^{-5}$
26	3,60	1,60	0,0022	0,002	$4,5 \cdot 10^{-5}$
27	3,30	1,65	0,0019	0,002	$3,0.10^{-5}$
Average	3,40	1,60	0,0020	0,003	$3,9 \cdot 10^{-5}$
Average:	K/Li = 80;	Na/Li = 1700;	Rb/Tl = 80;	Na/K = 2,1	

Enclosing rocks (micaceous quartzites)

	Na	K	Li	Rb	Tl	Rb/Tl	Na/K	Na/Li	K/Li
28 (Quartzite at contact)	0,120	1,50	0,0010	0,0017	$2,5 \cdot 10^{-5}$	68	0,07	120	1500
29 (Quartzite 100m from contact)	0,080	0,80	0,0014	0,0005	$1,0.10^{-5}$	50	0,01	80	800

Note: Comma represents decimal point.
$2,5 \cdot 10^{-5}$ represents 2.5×10^{-5}.

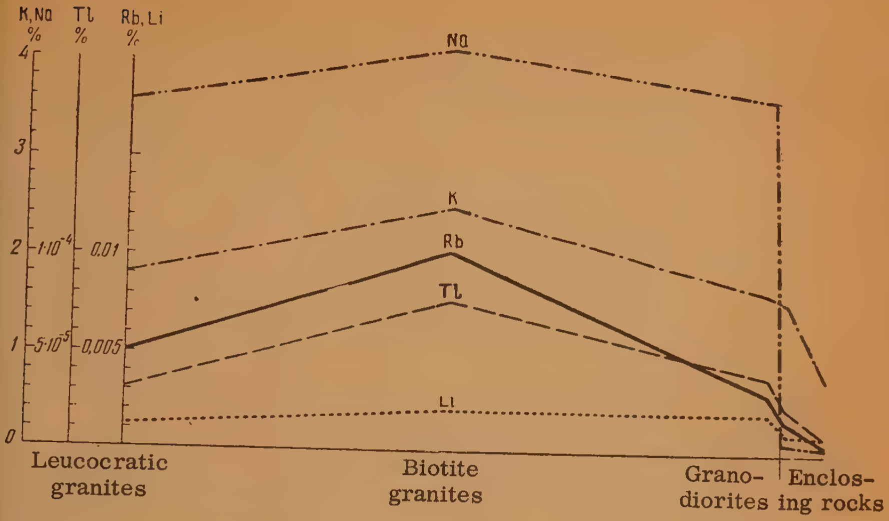

Fig. 1. Average K, Na, Rb, Li and Tl content in the rocks of the Turgoyak pluton

clarke for this element. In the enclosing rocks (micaceous quartzites) the amount of lithium is 0.001% (Table 3 and Fig. 1).

Rubidium. The rubidium content in the leucocratic granites varies from 0.002 to 0.008%. This is due to the extreme nonuniformity of these rocks. The low Rb content (0.002%) is characteristic of leucocratic granites poor in microcline and biotite (for example, sp. 4, table 3). The average Rb content in the leucocratic granites is 0.005%, which is lower by one order than the clarke of this element in granites as given by Ahrens [7]. In the biotite granites the average rubidium content is higher and amounts to 0.01%. This is lower than Ahrens' clarke but higher than the clarke given by Eramets and Wager [5].

The variation in rubidium content in the biotite granites is slight, from 0.008% to 0.014%. A definite pattern is observed: the rubidium content in biotite granites increases at first towards the contact and then with change to granodiorites, decreases. In the granodiorites its average content is considerably lower than the clarke, being only 0.003%. In the enclosing rocks, the rubidium content is considerably lower than in the granitoids. In the micaceous quartzites near the western contact of the pluton, it is 0.002%, and only 0.0005% 100 m farther west (Table 3, Fig. 1).

In general, the rocks with high potassium content are also enriched in rubidium, indicating a close geochemical relationship between the two elements.

Thallium. The average thallium content in leucocratic granites is 0.30 ppm, which is lower by one order than the clarke of thallium in granites as given by Shaw.

The thallium content in leucocratic granites ranges widely between 0.15 and 0.52 ppm. The specimens with the higher Rb (and K) content have higher Tl content, and vice versa (Table 3). The average Tl content in biotite granites is about 2.5 times higher than in the leucocratic granites (0.75 ppm) but still lower than Shaw's clarke for granites. In the granodiorites the Tl content drops to 0.39 ppm. In the enclosing rocks, it continues to decrease, but at a slower rate than the Rb content. In the hornfelses the amount of Tl is near the limit of sensitivity of analysis--0.1 ppm. The micaceous quartzites contain 0.2 ppm Tl. The same amount was found in the granodiorites near the contact. One hundred meters from the granodiorite-quartzite contact, the Tl content in the latter diminishes to 0.1 ppm.

Thus, the content of all alkali metals and of Tl increases from the leucocratic granites to the biotite granites, but diminishes (except for Li) again in the granodiorites, and, in the case of some elements (for example, for Rb), to amounts smaller than those present in the leucocratic granites. This may be explained by the fact that during the formation of the Turgoyak pluton the alkalies were carried out from the central into the peripheral zones of the pluton. The possibility of loss of the alkalies during hybridization has been noted by a number of investigators (O. S. Polkovaya [8], V. S. Koptev-Dvornikov [2], D. S. Korzhinskii [9] and D. L. Reynolds [10]). The central intrusive phase of the leucocratic granites was impoverished in the alkalies during this process, and they became fixed in the biotite granites. In the granodiorites the decrease in the alkalies and Tl as compared with the leucocratic granites is due, apparently, to the dilution of these rocks by the elements introduced from the enclosing rocks (Mg, Fe, Ca).

The removal of the alkali metals and Tl into the enclosing rocks is indicated by their somewhat higher content at the contacts and near them than in the more distant areas. In general, however, the content of these elements in the enclosing rocks is considerably lower than in the granodiorites.

The migration of the alkalies from the central parts of the pluton into the marginal parts varied in intensity. The Na/K ratio in all rocks of the pluton remains approximately constant ($\sim$2), while in the enclosing rocks at the contact it drops to 0.1.

The behavior of lithium in the rocks of the Turgoyak pluton is somewhat different from that of the other alkalies. Table 3 shows the ratio of the common alkalies to lithium.

The observed decrease in the ratio of K and Na to Li from the central to the peripheral parts of the pluton testifies to the greater mobility of Li as compared with K and Na. This is due, apparently, to the smaller ionic radius of Li. Evidently the leucocratic granites have no minerals with crystal lattices suitable for the fixation of lithium. At the same time, because of the nearness of the ionic radii of Li, Mg, and Fe^{2+}, lithium is capable of replacing these elements in the biotites and hornblendes.

It is interesting to note also that there are certain differences in the behavior of Rb and Tl. The Rb/Tl ratio in the rocks of the Turgoyak pluton decreases regularly from the leucocratic granites, in which it is 180, to the biotite granites (130), and further, to the granodiorites (80). The decrease in this ratio shows that in the process of migration of the alkalies and Tl from the granitic magma, thallium was more mobile and enriched (relative to Rb) the peripheral parts of the pluton. In the enclosing rocks the Rb/Tl ratio is 68 at the contact, but 100 m to the west, it drops to 50. Thus, during metasomatism thallium behaves as a more mobile element than rubidium.

The characteristics of behavior of Rb and Tl may be explained by the difference in their electronegativity. The basic laws governing the distribution of the elements in minerals were formulated by Goldschmidt [6]. According to him, two ions may replace each other in crystal lattices if their ionic radii do not differ by more than 15%. The shortcoming of this rule is that it was derived for purely ionic structures and underestimated the effect of polarization. In recent years the electronegativity of the ions has been taken into consideration in determining the rules of ionic substitution.

It was shown by A. E. Ringwood [11] that of two ions equal in charge and size the ions with the lower electronegativity will enter into a structure with a strongly electronegative anion, for this results in strong ionic bonding. The element with higher electronegativity, on the other hand, will form a weaker covalent-ionic bond (the polarity of the bond will be less).

Ramberg [12] gave the following rule for the silicates: of the many possibilities, those are realized in the silicates which lead either to the maximum or the minimum polar bonding, i. e. ionic or covalent bonds predominate among the silicates.

The change from the nesosilicate to the tectosilicate structure is accompanies by an increase in the electronegativity of oxygen. Paralleling this, there is a tendency towards diadochic replacement of the cations with lower electronegativity. Indeed, during magmatic differentiation, cations with high electronegativity, such as Fe and Mg, are the first to form structures. At the end of the process the tectosilicates contain mainly cations with low electronegativity (alkalies) (G. B. Bokii, S. S. Batsanov [13]).

Of the two elements, Rb and Tl, the latter has the higher electronegativity: Tl -- 1.5, Rb -- 0.8 (according to Pauling). Therefore, rubidium will enter more readily into the structure of potassium feldspars and biotite and form more strongly polar bonds. Thallium, on the other hand, because of its weaker bonding in these silicates, will be carried out more readily to the peripheral zones of the pluton.

The electronegativity of the anion in biotite is lower than in microcline. Therefore, Tl will more readily enter into the biotite than the microcline structure. It was discovered during the present research that the varieties of rocks enriched in biotite contain more Tl than those which have little biotite.

In conclusion the author expresses his deep gratitude to the supervisor of this research, K. K. Zhirov, and also to N. T. Voskresenskii, D. N. Ivanov, and V. I. Lebedev for their advice on the method of determination of Tl and the alkali metals.

Summary

1. The granitoids of the Turgoyak pluton were formed as a result of assimilation of the invaded rocks by the leucocratic granitic magmas.

2. The content of the alkalies (Na, K, Li, Rb) and of Tl increases from the leucocratic granites (central parts of the pluton) to the biotite granites and decreases, with the exception of Li, in the granodiorites (near the contact zones of the pluton).

3. In the process of formation of the Turgoyak granitoids, the alkalies and Tl were carried out into the peripheral zones of the pluton and into the enclosing rocks. The removal of these elements varied in intensity. The most mobile were lithium, potassium, and thallium.

4. The decrease in the Rb/Tl ratio in the rocks of the Turgoyak pluton from 180 in the leucocratic granites to 70 in the granodiorites is characteristic and indicates the greater mobility of Tl.

The difference in the behavior of Rb and Tl is probably related to the difference in the electronegativity of these elements.

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DISTRIBUTION OF URANIUM IN THE ROCKS OF THE LOVOZERO ALKALI MASSIF

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Until recently there were almost no data in the literature on the behavior of uranium in nepheline syenites. It was known that thorium rather than uranium minerals are characteristic of these rocks. Inasmuch as there are no uranium deposits areally or genetically related to nepheline syenites, and these rocks do not carry independent uranium minerals (uraninite, urano-thorite, etc.), such as occur in acid rocks, it was believed for a long time that nepheline syenites are poor in uranium as compared with acid rocks. Fersman [1] believed that while thorium "enters mainly into sodic and alkalic magmas, i. e. into agpaitic or miaskitic rocks, uranium is practically absent from these magmas and when present is associated with potassium." V. M. Goldschmidt [2] wrote: "The concentration of uranium (and of its daughter elements) is usually much higher in the acid granitic magmas than in syenites and nepheline syenites."

In the manuscript of his doctoral dissertation, "Content and geochemical pattern of distribution of radioactive elements in some of the granites of the USSR" [3], L. V. Komlev gives figures for the average uranium content in the nepheline syenite intrusives of the Urals and the Kola Peninsula. He states that nepheline syenites are "as a rule poor in uranium" except for certain varieties of rocks in the massifs formed from magmas enriched in volatile components.

There is a report by Sörensen and Bondam [4] on the distribution of uranium in the Ilimaussaq massif of Greenland. The authors discuss only the relatively high radioactivity of the zones altered during the last stages of formation of the massif and do not mention the behavior of uranium in the unaltered nepheline syenites. Thus, at present the question of the nature of the geochemical behavior of uranium in nepheline syenites cannot be considered adequately investigated. The question is of undoubted interest and the author has taken the first steps towards its clarification. The Lovozero nepheline syenite massif, selected as the object of the investigation, is located on the Kola Peninsula to the east of the Khibina tundra. Its area is 650 km^2. It is a multiphase intrusion composed of several varieties of nepheline syenites. The enclosing rocks are Archean gneisses and a Devonian volcanic-sedimentary sequence [5]. The age of the massif, according to the geological data [5], is Middle Paleozoic, and its absolute helium age is 266 million years [6].

According to current ideas the massif was formed in four intrusive phases [5, 7].

The rocks of the first and oldest phase are poikilitic nepheline syenites, porphyritic nepheline syenites, nepheline syenites, equigranular nepheline syenites and subordinate foyaites and urtites. All of these rocks occur as xenoliths in the rocks of the second and third intrusive phases. The rocks of the first phase have the lowest agpaitic coefficient of all the nepheline syenites in the massif (0.8 - 1.23).

The complex of lujavrites, foyaites, and urtites of the second intrusive phase forms the largest part of the massif. These rocks occur as gently dipping tabular bodies and are easily traced through the entire massif. The upper part of the complex is composed of repeated three-layer sequences composed in almost every case of urtite, lujavrite, and foyaite.

The rocks of the third phase overlie those of the second phase. The third intrusive phase is composed of lujavrites, juvites, and eudialytites. The main role here is played by the eudialyte lujavrites occurring in tabular bodies which are extensive but less continuous than in the second intrusive phase. The porphyritic lujavrites are found as separate tabular and lenticular bodies at the boundary between the second and third phases and also as discordant bodies cutting the eudialyte lujavrites. The porphyritic lujavrites are sometimes enriched in lovozerite. The eudialytites have limited distribution and occur as irregular masses and lenses in the eudialyte lujavrites.

To the rocks of the third phase, which are younger than the eudialyte syenites, V. I. Gerasimovskii [7] refers amall bodies of tawites and poikilitic sodalite syenites.

The fourth phase is composed of monchiquite, fourchite, alkali basalt, and tinguaite dikes, which cut all the rest of the rocks.

A characteristic geochemical feature of the Lovozero massif is the enrichment of its rocks in the alkalies (especially sodium) and their principal minerals are nepheline, potassium-sodium feldspar, sodalite, arfvedsonite, and aegirine. Sodium occurs also in a number of other minerals.

The important role of Zr, Ti, Nb, RE, Fe, and Se, which enter into the composition of both essential and accessory minerals, should be noted.

For the study of the geochemistry of uranium in the Lovozero alkalic massif, it was necessary to determine the distribution of this element in the rocks of each of the four intrusive phases. For the determination of uranium the author used the rapid and quite accurate method developed by P. I. Vasil'ev and R. L. Podval'naya [8]. This method requires separation of uranium from Th, RE, and other elements interfering in the luminescence analysis. It is recommended for the determination of thousandths and ten thousandths of one percent of uranium. The accuracy of the method under the conditions of the present research was 25% relative.

The author analyzed 60 samples of the Lovozero rocks. The data are presented in the table.

The results of the investigation indicate that even the relatively small amount of material analyzed reveals a definite pattern in the distribution of uranium in the rocks of the Lovozero alkalic massif.

With the exception of tawite and poikilitic sodalite syenites, for which the data are still insufficient, the rocks of the massif show an increase in

Distribution of Uranium in the Rocks of the Massif

No.	No. of sample	Name of rock	Sampling locality	Uranium content in g/ton
		Rocks of the first intrusive phase		
1	69	Equigranular nepheline syenite	Mt. Ninchurt	10
2	139	Equigranular nepheline syenite	Mt. Ninchurt	10
3	68	Porphyritic nepheline syenite	Mt. Ninchurt	13
4	183	" " "	Mt. Alluaiv	7
5	185a	" " "	"	15
6	193	" " "	"	15
7	77	Poikilitic nepheline syenite	Mt. Punkaruaiv	6
8	72	" " "	"	4
9	75	Poikilitic nepheline syenite	"	6
10	66	" " "	Mt. Suoluaiv	12
11	188a	" " "	Mt. Alluaiv	8
12	196	" " "	"	9
13	431	" " "	Tavaiok River	7
14	66a	" " "	Mt. Suoluaiv	16
	–	Average for the rocks of the first phase		9.9
		Rocks of the second intrusive phase		
15	34	Melanocratic lujavrite	Mt. Alluaiv	11
16	28	" "	Mt. Karnasurt	11
17	23	Mesocratic lujavrite	"	18
18	26	" "	"	16.5
19	26b	Leucocratic lujavrite	"	18
20	8	Hornblende lujavrite	"	12
21	124	" "	Mt. Alluaiv	13
22	19	" "	Mt. Karnasurt	13
23	264	Lujavrite with loparite	Mt. Alluaiv	10
24	190	" "	Mt. Alluaiv	21
25	362	" "	Mt. Parguaiv	11
26	142	Urtite	Mt. Karnasurt	12
27	276	"	Mt. Alluaiv	13
28	187	Ijolite-urtite	"	9
29	14b	"	Mt. Karnasurt	4.5
30	132	"	Mt. Alluaiv	11
31	262	Urtite with loparite	"	55
32	363	" "	Mt. Parguaiv	30
33	268	Apatite urtite with loparite	Mt. Alluaiv	15
34	XIX	"	Kuftn'yun River	22
35	272	Foyaite	Mt. Alluaiv	20
36	143	"	Mt. Karnasurt	19
37	144	"	Mt. Karnasurt	20
38	130	"	Mt. Alluaiv	16
39	38	"	Mt. Alluaiv	14
		Average uranium content in the rocks of the second phase		15.3*

* The average uranium content in the rocks of the second and third intrusive phases were computed with the abundance of the individual varieties of nepheline syenites in these phases being taken into account.

No.	No. of sample	Name of rock	Sampling locality	Uranium content in g/ton
		Rocks of the third intrusive phase		
40	165	Eudialyte lujavrite	Mt. Alluaiv	20
41	168b	" "	"	20
42	168a	" "	"	20
43	50a	" "	Mt. Karnasurt	16
44	49	Eudialyte lujavrite	"	20
45	160	" "	Mt. Alluaiv	17
46	245	" "	"	19
47	170	Porphyritic lujavrite	"	13
48	XXI	" "	Mt. Flora	31
49	249	" "	Mt. Alluaiv	27
50	246	Porphyritic juvite with loparite	"	21
51	263	Lovozerite porphyritic lujavrite	Mt. Karnasurt	89
52	106	Lovozerite porphyritic lujavrite	Mt. Vavnbed	75
53	110	Eudialytite	"	29
54	430	Tawite	Tavaiok River	49
55	266	Pokilitic sodalite syenite	Tyulbn'yunuai River	13
56	92	"	Uel'kuai River	10
57	141	"	Chinglusuai River	28
58	104	"	Mt. Vavnbed	11
		Average for the rocks of the third phase		19.7
		Rocks of the fourth intrusive phase		
59	XXII	Monchiquite	Mt. Alluaiv	3.5
60	1393	"	Mt. Karnasurt	2
		Average for the rocks of the fourth phase		2.8

uranium content from the first intrusive phase to the third.

In the dike rocks (monchiquites), the content of uranium is lower than in the nepheline syenites and equals 2-3.5 g/ton. The monchiquites, fourchites, and alkalic basalts are dikes of the lamprophyre type in relation to the nepheline syenites of the Lovozero massif. They have a more basic composition and belong to the group of alkalic gabbroids and basaltoids. It is possible that the lamprophyres of the granitic massifs also have lower uranium content than the parent rocks. If this is true, the explanation must be sought in the conditions of formation of lamprophyre dikes, which are far from being clear at present.

The distribution of uranium in the rocks of the Lovozero massif must now be reviewed. It may be noted that in the rocks of the second and third intrusive phases composing the larger part of the massif, the variation in the uranium content from one sample to another is insignificant. In the eudialyte lujavrites it does not deviate by more than 16% from the average; in the foyaites and aegirine lujavrites it deviates by 22 and 27%, respectively (see Table).

In the poikilitic and porphyritic nepheline syenites of the first phase, the differences between the individual samples are larger and amount to 53% and 44%, respectively, of the average value. However, the uranium content in the samples from a xenolith or from several xenoliths near each other is, in most cases, very much the same. In the samples from Mt. Ninchurt the amount of uranium ranges from 10 to 13 g/ton, in those from Mt. Punkuruiv, 4 to 6 g/ton, in those from Mt. Suoluaiv, from 12 to 14 g/ton, while three out of five samples from Mt. Alluaiv contain from 7 to 9 g/ton of uranium. It is possible that the irregular distribution of uranium in the xenoliths from the different areas of the Lovozero massif may be explained by the different effect on these areas of the younger magmatic intrusions.

A characteristic feature of the Lovozero massif is the presence among its rocks of varieties relatively enriched in uranium as compared with its average content in the individual intrusive phases.

The rocks which stand out against the general background are tawite, containing 44 g/ton of U, and the porphyritic lovozerite lujavrite, containing 82 g/ton U. As compared with the eudialyte lujavrites predominating in the third phase and containing on the average 19 g/ton of uranium, this element is enriched in eudialytites carrying 29 g/ton U and porphyritic murmanite lujavrites with 29 g/ton U. In the rocks of the second phase, the high uranium content is found in some samples containing loparite, i. e., in urtite (two samples) with 30-53 g/ton U, in apatite urtite with 22 g/ton U, and in lujavrite with 21 g/ton U.

The author has found that loparite, lovozerite, and to a less extent murmanite and eudialyte are relatively rich in uranium: loparite (9 samples) contains 0.015-0.037% U, unaltered black loparite (one sample), 0.155% U, and eudialyte (seven analyses) 0.0038 - 0.0082% U. The presence of some of these minerals in the rocks listed above is evidently responsible for the greater or less enrichment in uranium.

In view of the above data and the relative abundance of each intrusive phase, the author concludes that the average uranium content in the Lovozero nepheline syenites is 16 g/ton.

Summary

1. There is a regular increase in the uranium content from the rocks of he first intrusive phase to those of the third and later phase.
2. The content of uranium in the monchiquite dikes of the lamprophyre roup (fourth intrusive phase) is much lower than in the nepheline syenites f the first three phases.
3. The rocks of each intrusive phase have a higher uranium content if hey contain lovozerite, loparite, or eudialyte.
4. The average uranium content in the nepheline syenites of the Lovozero massif is 16 g/ton, i. e. four times as high as the average uranium ontent in granites.

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CHEMICAL COMPOSITION OF THE GASES OF THE VOLCANO EBEKO

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At present in the Soviet Union many active Kamchatkan volcanoes are under systematic observation, which includes the study of their gases.

Especially interesting are the chemical characteristics of gases of primary fumaroles connected with volcanic vents, for they reflect to a large degree the composition of the magmatic gases. Undoubtedly the proportions of the components in the gas mixture emitted at the surface are different from those in the primary magmatic gases, but nevertheless analyses of these mixtures do give us some idea of the composition of the primary magmatic gases.

The fumaroles of the volcano Ebeko (Kurile Islands), the composition of whose gases has been little studied, are of considerable interest. In the literature there are a few data on the chemical composition of thermal and crater lake waters and of the gases escaping from them, as well as of the fumarolic sublimates of the upper crater of Ebeko [2].

However, no studies of gases and sublimates collected directly from the fumaroles at different parts of the volcano have been made and the chemistry of the gases of Ebeko remained unknown.

Ebeko is located in the northern part of Paramushir Island and rises 1138 m above sea level. The summit of its central cone bears three craters adjacent to one another and of almost the same size (250-300 m in diameter).

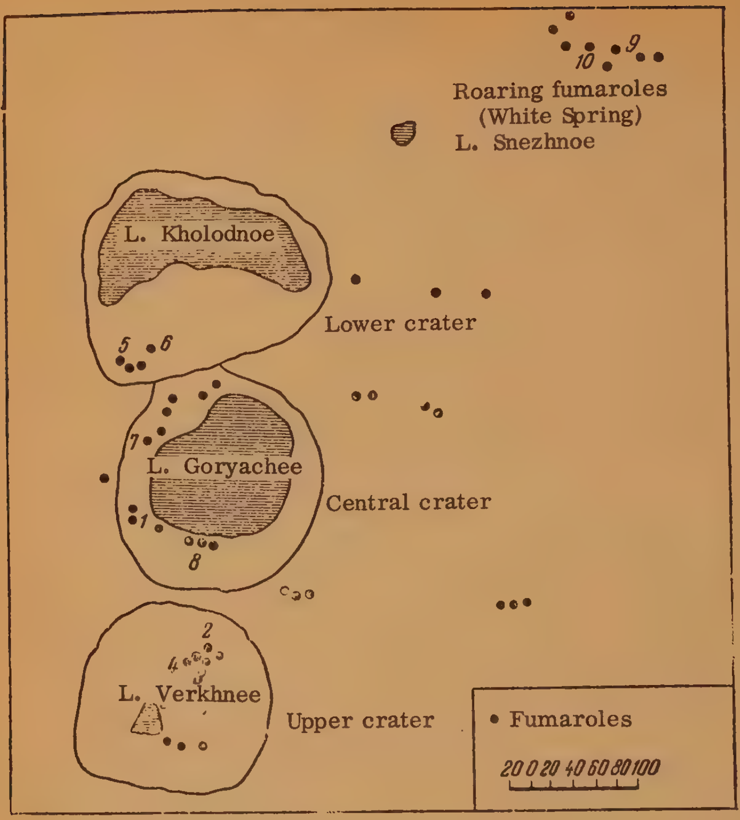
On the bottoms and walls of the craters and on the slopes of the cone there are numerous large fumaroles. Even a cursory examination shows that the fumaroles of Ebeko have several characteristics in common:

1) all fumaroles emit large quantities of sulfur, which is deposited about their vents and gradually builds up sulfur mounds;

2) the gases are ejected from the openings in powerful jets with velocities up to 60 m/sec;

3) the temperature of the gases at the vents does not exceed 120°C.

The gases and sublimates of ten fumaroles were studied in detail. About 300 samples were collected and analyzed. Fumaroles Nos. 3, 4, 5, 7, 8, 9 and 10 are located on sulfur mounds whose lower layers have been compacted into a greenish-gray mass. At the vents very rapidly accumulating small sulfur crystals form fresh yellow incrustations. The gas admixed to the vapor escapes from the vents with a roar, with velocities up to 50 m/sec.



Distribution of principal fumaroles on Ebeko

The samples were collected and analyzed by the method previously used in the investigation of volcanic gases in Kamchatka [3]. The analyses of free fumarolic gases collected after condensation of water vapor at 20-30°C are given in Table 1. From 3 to 8 samples were collected from each fumarole, and the figures are averages of the corresponding number of analyses. The determinations of H_2S, SO_2, and HCl were made by titrimetry, of CO_2 by gravimetry, and H_2, CO, CH_4, N_2, and O_2 were determined on the VTI apparatus.

Table 1 shows that concentrations of nitrogen and oxygen in the fumarolic gases of Ebeko are very low, negligible by comparison with other volcanic gases. The very low content of atmospheric air sharply distinguishes them from the gases of the Kamchatkan volcanoes, in which the author and other investigators found the content of nitrogen and oxygen to be 90%. As an illustration, we cite the analyses of gases collected from the central fumaroles of the volcano Sheveluch and from the lava flow of Bezymyannyi (1956).

The amount of oxygen and nitrogen and the O_2/N_2 ratio of Ebeko is lower in all cases but one than in the air. The low oxygen content is easily explained by its expenditure in oxidation.

Table 1

Chemical Composition of Gases of Ebeko with Water Vapor Omitted (vol. %)

No. of fumarole	T. of fumr. °C	H_2S	SO_2	CO_2	HCl	H_2	CO	CH_4	O_2	N_2	H_2O g/l	$H_2S : SO$
Upper fumarole												
2	96	1,33	0,115	93,72	0,89	0,0	0,3	0,3	1,4*	0,2*	30,0	11,57
3	114	0,40	0,085	95,69	0,07	0,4	0,0	0,0	0,6	2,5	3,5	4,7
4	109	0,41	0,080	97,18	0,04	0,0	0,1	0,2	0,3	1,7	3,0	5,1
Central crater												
1	95	0,02	0,05	89,13	0,12	0,0	0,1	0,3	1,5	8,6	16,0	0,44
7	101	0,22	0,08	94,38	0,27	0,0	0,0	0,0	0,1	4,7	1,6	2,7
8	102	0,26	1,40	90,78	2,90	0,0	0,0	0,0	0,1	4,4	3,0	0,2
Lower crater												
6	94	0,25	0,04	98,51	0,94	0,0	0,0	0,0	0,0	0,0	6,0	6,1
5	110	0,55	0,24	96,51	0,08	0,0	0,0	0,0	0,2	1,4	3,0	2,3
White Spring												
9	102	traces	2,6	93,85	0,15	0,0	0,0	0,0	0,4	3,0	5,0	
10	112	traces	3,0	96,39	0,23	0,0	0,0	0,0	0,2	2,7	5,0	

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* Possible error
Comma represents decimal point.

Table 2

Chemical Composition of Gases of Sheveluch and Bezymyannyi (vol. %)
(average of 3 analyses)

Date of sampling	No. of fumarole	Temperature of fumarole, °C	H_2S	SO_2	CO_2	H_2	O_2	N_2
		Sheveluch						
Aug. 2, 1956	Central fumarole	270	0,0	2,35	12,9	0,5	10,0	73,4
		Bezymyannyi						
Sept. 5, 1956	1	100	0,04	0,06	12,2	0,0	15,2	62,5
Sept. 9, 1956	2	200	0,21	0,24	16,5	0,0	12,5	71,7
Sept. 10, 1956	3	100	2,40	0,07	14,3	0,0	13,8	59,4

Note: Comma represents decimal point.

No. of fumarole	In air	No. 2	No. 3	No. 4	No. 1	No. 7	No. 8	No. 6	No. 5	No. 9	No. 10
	0. 26	?	0. 24	0. 18	0. 17	0. 02	0. 23	-	0. 13	0. 13	0. 07

Table 1 shows that carbon dioxide, whose content ranges from 89 to 98.5%, is the main component of the gases.

Hydrogen sulfide and SO_2 were determined in all fumaroles, and it was found that their ratio varies. Fumaroles No. 9 and 10 emit SO_2 almost exclusively (its content reaches 3%) and the concentration of H_2S is negligible. The area of fumaroles Nos. 9 and 10 is the hottest part of the volcano and the number and strength of its fumaroles is considerably greater than in the upper, central, and lower craters. Thus, the predominance of SO_2 may be related to the temperature regime.

Table 3

Chemical Composition of Sublimates of Ebeko (in mg/l of sublimate)

No. of fumarole	Tempera- of fumarole, °C	Sublimate (g/l of gas)	pH	SO_3^{2-}	Cl^{1-}	NH_4^-	Polythionic acids
Upper crater							
2	96	30,0	1,88	64	109	0,0	0
3	114	3,5	1,02	39	311	0,0	0
4	109	3,0	0,91	18	574	0,0	0
Central crater							
1	95	16,0	2,20	249	23	0,3—0,6	32
7	101	1,6	2,65	157	120	0,0	0
8	102	3,0	0,50	69	13701	1—2	0
Lower crater							
6	94	6,0	2,65	157	92	0,0	0
5	110	3,0	1,55	58	671	0,3—0,6	0
Region of White Spring							
9	102	5,0	1,40	3508	49	0,3—0,6	154
10	112	5,0	1,30	6956	878	1—2	32

Note: Comma represents decimal point.

In the gases of the fumaroles located in the three craters, hydrogen sulfide predominates over SO_2 except in fumaroles Nos. 1 and 8. It should be noted that the gas phase contains no SO_3.

An interesting peculiarity of the gases of Ebeko is the presence of HCl, whose concentration in fumarole No. 8 reaches 3%.

To characterize the fumarolic gases more fully, the chemical composition of their sublimates is given in Table 3.

As Table 3 shows, all sublimates have low pH, ranging from 2.65 to 0.50. All sublimates contain HCl, those of fumarole No. 8 having the maximum amount of 14 g/l, which is nearly equivalent to a 0.5N solution of HCl.

All sublimates contain $SO_3{}^{2-}$, the maximum content being in fumaroles Nos. 9 and 10. This is in good agreement with the percentage of SO_2 in the gas phase of these fumaroles (Table 1).

The sublimates of the volcano are of considerable interest because they contain polythionic acids. There are statements in the literature concerning the possibility of formation of polythionic acids in the sublimates of the low temperature fumaroles containing sulfurous compounds [4, 5]. Zavaritskii's note on the presence of polythionates in the sublimates of the volcano Avacha [6] is the only reported occurrence of these compounds in our volcanoes of Kamchatka and the Kuriles. On Ebeko the author found these acids only in the sublimates of fumaroles Nos. 1, 9 and 10; they are absent from all other fumaroles. This may be related to the abundance of SO_2 in the sublimates of these three fumaroles, which creates favorable conditions for the formation of polythionic acids [7]. An assay for the polythionic acids in the sublimates was made by the method of Deines [4].

The data of Table 1 show that fumarole No. 2 has higher contents of H_2S, SO_2, CO_2, and HCl than the fumaroles of the upper crater.

The content of soluble components in fumaroles Nos. 1, 2 and 6, which have small discharge and low temperature (below boiling temperature of water), should be lower than in the fumaroles with temperatures over 97°C, but this is not confirmed by the data of Table 1.

This discrepancy may be ascribed to the omission of water vapor from Table 1, whose figures, therefore, do not reflect the actual relationship among the components of the gas escaping at the surface. For this reason, gas analyses with water vapor included are presented in Table 4.

The tabulated data show that the concentration of H_2S, SO_2, CO_2, and HCl in the low temperature fumaroles of a given region is lower than in the fumaroles with temperatures exceeding the boiling point of water. This is explained by the solution of these components in the sublimate, which, as temperature falls, becomes separated from water vapor before the eruption and is absent, therefore, even from the first gas jet.

To compare the composition of fumarolic gases and thermal waters, the composition of the gases expressed in grams per liter of sublimate (gas phase included) is presented in Table 5.

Summary

1. The principal components of the fumarolic gases of Ebeko are H_2O, CO_2, HCl, H_2S, and SO_2.
2. The concentration of oxygen and nitrogen in these gases is negligible, indicating an almost complete absence of contamination of the samples with atmospheric oxygen and their high quality.

Table 4

Chemical Composition of Gases of Ebeko Including Water Vapor (vol. %)

No. of fumarole	Temp. of fumarole, °C	H_2S	SO_2	CO_2	HCl	H_2	CO	CH_4 etc.	O_2	N_2	H_2O
Upper crater											
2	96	0,0346	0,003	2,44	0,026	0,0	0,0078	0,008	0,036	0,005	97,39
3	114	0,0800	0,017	19,14	0,035	0,08	0,0	0,0	0,012	0,5	79,98
4	109	0,086	0,017	20,50	0,303	0,0	0,022	0,04	0,066	0,35	78,60
Central crater											
1	95	0,001	0,002	4,45	0,007	0,0	0,005	0,01	0,075	0,43	95,00
7	101	0,058	0,021	25,01	0,076	0,0	0,0	0,0	0,026	1,24	73,43
8	102	0,055	0,030	19,15	7,586	0,0	0,0	0,0	0,023	0,93	71,90
Lower crater											
6	94	0,026	0,004	10,34	0,103	0,0	0,0	0,0	0,0	0,0	89,5
5	110	0,116	0,093	20,36	0,044	0,0	0,0	0,0	0,04	0,29	79,1
White Spring											
9	101	traces	0,440	13,42	0,024	0,0	0,0	0,0	0,057	0,43	85,6
10	112	traces	0,563	13,77	0,071	0,0	0,0	0,0	0,030	0,39	85,6

Note: Comma represents decimal point.

Table 5

Composition of Fumarolic Gases in g/l H_2O

No. of fumarole	Temp. of fumarole, °C	H_2S	SO_2	CO_2	HCl	CH_4	O_2	N_2
2	96	0,7	0,1	62,0	0,5	0,07	0,7	0,07
3	114	1,9	0,8	591,6	0,9	0,0	0,3	9,8
4	109	2,2	0,8	646,3	7,8	0,5	1,5	7,0
1	95	0,02	0,09	115,8	1,5	0,14	1,5	7,1
7	101	1,5	1,01	842,7	2,06	0,0	0,6	26,4
8	102	1,5	1,5	660,3	214,4	0,0	0,6	20,1
6	94	0,6	0,18	287,6	2,3	0,0	0,0	0,0
7	110	2,8	4,3	638,0	1,1	0,0	0,9	5,8
9	102	0,0	18,8	388,1	0,56	0,0	1,2	7,8
10	112	0,0	23,8	398,7	1,72	0,0	0,63	7,2

Note: Comma represents decimal point.

3. As was to be expected, the fumarolic gases with surface temperatures lower than the boiling point of water are poor in water-soluble components (HCl, SO_2, CO_2, and H_2S) because of condensation of water vapor before emission at the surface.

4. The peculiarity of the gases of Ebeko (relatively low temperature) is the considerable content of SO_2 and HCl, typical of gas mixtures emitted at higher temperatures directly from the lavas at the moment of eruption (Klyuchevskii, Sheveluch, and other volcanoes).

5. For the first time since the beginning of investigations of fumarolic gases of the Kamchatka and Kurile volcanoes, polythionic acids were found and quantitatively determined in the gases of Ebeko.

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DISCUSSION

ON THE THERMODYNAMIC POTENTIALS OF A SYSTEM WITH COMPLETELY MOBILE COMPONENTS PROPOSED BY D.S. KORZHINSKII*

D. S. Korzhinskii has proposed to use as the thermodynamic potentials in the study of systems some of whose components are completely mobile the functions

$$Z_0 = Z - \sum_{p=f}^{p=k} \mu_p m_p, \tag{1}$$

where the components f to k are "completely mobile."

The total differential of function Z_0 can be written:

$$dZ_0 = -SdT + Vdp + \sum_{i=a}^{i=e} \mu_i dm_i - \sum_{p=f}^{p=k} m_p d\mu_p. \tag{2}$$

If the system is placed under such conditions that T, p, $m_a \ldots m_l$, $\mu_f, \ldots, \mu_k$ are constant, then, according to (2):

$$dZ_0 = 0$$

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*Academician D. S. Korzhinskii, in his papers and in a monograph [1-5, 10], proposed the use of a family of special thermodynamic potentials in the study of the problems of paragenesis of minerals which indicate that the systems under investigation contain completely mobile components. Some of the properties of these functions as presented by Korzhinskii have been questioned in print by Corresponding Member of the Academy of Sciences, USSR, V. A. Nikolaev [6-8] and by Professor A. V. Storonkin [9].

The Chemical Thermodynamics Committee of the Division of Chemical Sciences, Academy of Sciences, USSR, heard and discussed Korzhinskii's report on the thermodynamic properties of the functions. V. A. Nikolaev participated in the discussion and A. V. Storonkin sent in his remarks. After additional discussion the Committee arrived at the conclusions which are presented in this note.

nd function Z_o may serve as a criterion of equilibrium, i. e. to the equibrium of the system (under the given conditions) will correspond the miniium of the function.

The critics of these propositions assert that functions Z_o are not thermomamic potentials, and that their use in the solution of thermodynamic roblems in geochemistry is not permissible and leads to erroneous nclusions.

Korzhinskii's propositions must be amplified by this definition of the mpletely mobile components, *f* ... *k* of a system. They are those comnents whose chemical potentials are among the equilibrium factors, tother with the masses of the inert components *a* ... *e*. This definition ffers from that given by Korzhinskii in his earlier works.

Let us discuss Korzhinskii's propositions in two stages without touching on their geochemical applications.

1. First, let us consider functions Z_o as characteristic functions independent of the inertness or mobility of the various components.

2. Then, let us consider functions Z_o as thermodynamic potentials of a stem with completely mobile components, using as the basic criterion of mplete mobility the condition that μ_p = const. (Korzhinskii's first finition).

1. The determination of the value of Z_o (1) is independent of the inertss or mobility of the components, so that this value is the function of the ate of the system for *any arbitrary* division of the components of the sysn into two groups. Functions Z_o are evidently characteristic for the inpendent variables *p*, *T*, $M_a \ldots m_e$, $\mu_f \ldots \mu_k$, since by using selected lependent variables any thermodynamic property of the system can be pressed by the partial derivatives of this function.

2. Considering the condition μ_p = const. as being possible for the comtely mobile components of the system, and using the definition of function and the fundamental equation $\delta Q \leqslant TdS$, we obtain for the sum of irrersible and reversible changes in the system:

$$dU \leqslant TdS - pdV - \delta A' + \sum_{i=a}^{i=k} \mu_i dm_i. \qquad (3)$$

ere *A'* ("useful work") equals *A* - $\int pdV$.

$$= dZ - d\left(\sum_{p=f}^{p=k} \mu_p m_p\right) = d(U - TS + pV) - d\left(\sum_{p=i}^{p=k} m_p \mu_p\right)$$

$$Z_0 = dU - TdS - SdT + pdV + Vdp - \sum_{p=f}^{p=k} \mu_p dm_p - \sum_{p=f}^{p=k} m_p d\mu_p. \qquad (4)$$

stituting the expression for *dU* (3) in equation (4), we get:

$$dZ_0 \leqslant - SdT + Vdp - \delta A' + \sum_{i=a}^{i=e} \mu_i dm_i - \sum_{p=f}^{p=k} m_p d\mu_p$$

and if $\underline{T}$, $\underline{p}$, $m_a \dots m_e$, $\mu_f \dots \mu_k$ are constant

$$dZ_0 \leqslant -\delta A'$$

Therefore, $\underline{Z}_0$ is a thermodynamic potential of the system under the given conditions.

Ya. I. Gerasimov, Chairman
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NEWS

FIRST "SCIENTIFIC READING" IN MEMORY OF V.I. VERNADSKII

It has been resolved by the members of the V. I. Vernadskii Institute of Geochemistry and Analytical Chemistry to meet annually on March 12, the day of Academician Vernadskii's birth, for a "Scientific Reading" program devoted to those phases of geochemistry which represent the development of Vernadskii's ideas.

The first "Scientific Reading" was held on March 31, 1959.

In the conference hall of the Institute, before a large audience of scientists, Academician A. P. Vinogradov read a paper on the Chemical Evolution of the Earth.

Academician Vinogradov discussed the mechanism of differentiation of terrestrial matter into atmosphere, hydrosphere and lithosphere. He documented his discussion by extensive material including his own experimental work on the geochemistry of H_2O, CO_2, N, and other vapors and gases which now constitute the earth's atmosphere and hydrosphere.

Vinogradov pointed out that the earth has retained only those gases, vapors and other volatiles which were chemically combined with the primordial matter of the earth. An exceptional role in the elucidation of the processes of differentiation has been played by the data on the isotopic composition of inert gases in rocks and meteorites. The study of the isotopic composition of inert gases showed that all of them were formed in the earth's crust as a result of various nuclear processes connected with the radioactive decay of U and Th or with cosmic ray activity.

The earth did not retain the inert gases of cosmic origin. The formation of the hydrosphere and atmosphere is the result of degassing of the earth's mantle during the entire course of its evolution. The process of degassing is related to the process of selective fusion of the material of the mantle and formation of the crust. On the basis of the regularities in the distribution of the elements, (especially the rare ones in the igneous rocks of the crust and mantle), the variation in isotopic composition of a number of elements in the igneous rocks, and, finally, on the basis of experiments on zonal melting of the silicates, Vinogradov suggested a mechanism of separation of the crust similar to that of zonal melting. The size of a planet or some other cosmic body determines the character of its chemical evolution. It is possible to estimate the thickness of the mantle required to produce a given concentration of an element in the earth's crust. The materials remaining after the selective fusion of the earth's mantle are the olivine rocks -- dunites. Academician Vinogradov touched in his paper on the nature of energy which maintains the process of degassing and zonal melting leading to the shell structure of the earth.

A. Kuznetsova

April 22, 1959.

Geokhimiya began publication in 1956 under the able editorship of A. P. Vinogradov. It is the Soviet counterpart of Geochimica et Cosmochimica Acta, having practically identical fields of interest and coverage and publishing approximately the same number of pages per year. With the great increase in geochemical research in the U. S. S. R., there have come into being a number of highly specialized journals in geochemistry and related fields. It is probably better to begin translating this more general journal first and follow with some of the more specialized ones if interest appears to justify this course of action and if the financial arrangements can be made.

An initial grant from the National Science Foundation in 1958 enabled the Geochemical Society to translate and publish the eight issues for that calendar year. These issues have been very well received by a growing list of subscribers in most of the countries of the Western world.

Many inquiries have been received concerning back issues (1956 and 1957) and continuation of the program for issues after 1958. The National Science Foundation has made additional grants for translation and publication of the issues for 1956, 1957 and 1959. These are being translated and issued as rapidly as they can be processed. Prices are the same as for the 1958 issues (see inside front cover). Subscriptions and orders for single copies should be sent to the Geochemical Society in care of the undersigned.

The National Science Foundation has continued to be most cooperative in this venture. They are continuing support of the project although subscriptions are too few to make it anything like self supporting thus far. It is hoped that subscribers will call attention of other interested workers to the availability of the translation of Geokhimiya so that these important research papers can be made more generally available to those interested in geochemical and related investigations.

Earl Ingerson
Translation Editor
Department of Geology
The University of Texas
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In matters of subscription for Geokhimiya refer to: Moskva K-104, Pushkinskaya, 23, Akademkniga. Chief Editor: A. P. Vinogradov. Editorial Council: V. I. Baranov, K. A. Vlasov, V. I. Gerasimovskii, D. S. Korzhinskii, A. A. Saukov, N. I. Khitarov (Responsible Secretary), V. V. Shcherbina (Deputy Chief Editor).

Geochemical News is an informal bi-monthly newsletter published by the Geochemical Society and sent without charge to all of its members. It contains news of the activities of the Society, such as summaries of Council Meetings, reports of committees and plans for the future. It also includes announcements of forthcoming meetings and symposia of interest to geochemists, personalia, announcements or short reviews of books of geochemical interest, information on translations and translation services, letters and short notes by members, etc.

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Geochimica et Cosmochimica Acta is the official journal of the Geochemical Society. It is an international journal interested in the broad aspects of geochemistry, both geographically and subject-wise; articles have been received from contributors from all of the (inhabited) continents.

New chemical data and interpretations involving chemical principles are emphasized. For example, papers in chemical mineralogy, petrology, oceanography and volcanology are acceptable, as are those in the chemistry of meteorites, whereas it would be suggested that those in descriptive mineralogy and volcanology, petrography, physical and biological oceanography and physical meteoritics, be sent to other journals specializing in these subjects.

Thus, the subject coverage is closely similar to that of Geokhimiya. Also, the number of pages published per year is of the same order of magnitude. Subscription prices are as follows:

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